NUCLEAR MAGNETIC RESONANCE STUDIES OF MOLECULAR MOTIONS IN LIQUIDS

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by

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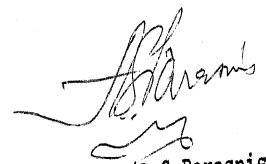
To

Dasharathi and Bhagabati

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This is to certify that the work reported in this thesis has been carried out under my supervision in this Department. No part of this work has been submitted elsewhere for a degree.

(A S Parasnis)
Professor of Physics

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Gandhi Jayanti

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SYMBOLS AND ABBREVIATIONS

The work presented here follow the symbols and units as described in the second edition of the booklet, *Quantities, Units, and Symbols* prepared and published by the Symbols Committee of the Royal Society in the year 1975 A.D. In labeling the figure axes and giving the column headings in the tables the prescription of the aforementioned booklet is followed.

The journal abbreviations are according to the American Institute of Physics' *Style Manual* published in April 1973. Other abbreviations follow the recommendations therein except that the term nuclear magnetic resonance is abbreviated as nmr.

A deviation from the prescribed SI units is the use of the traditional H for the magnetic induction or magnetic flux density rather than the prescribed B and also to loosely call it the magnetic field.

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In understanding the liquid state the study of the motion of the constituent atoms and molecules is of great importance. The translational and rotational motions of the constituents modulate the various interactions, and also the positional and motional autocorrelations which are amenable to nmr. Other advantages of the nmr technique are that it is a non-destructive method of investigation of the substance *in situ* and that although the help of models is required to be taken due to unsuitable time scales involved, the information obtained through nmr is quite significant in view of the present state of knowledge about the molecular dynamics in molecular liquids. Measurement of spin-lattice relaxation time and of self-diffusion coefficient of various neat compounds by using pulsed nmr technique as a function of molecular kinetic energy and their analysis provides valuable information such as the translational, reorientational, rotational and exchange correlation times, the extent of translation-rotation coupling, the effect of intramolecular group motion on

the entire molecular motion, the effect of molecular shape, size, inertia (mass, moment of inertia),dipole moment on the various motions *etc*..

A brief account of the principle of nmr with emphasis on the pulsed nmr measurable parameters is given in Chapter 1 of this thesis. The various relaxation mechanisms discernible are described. The importance of the spin-rotation interaction and the magnificent ability of the nmr technique to give information about the angular momentum correlation time are particularly emphasised. Self-diffusion coefficient, a measure of the linear velocity autocorrelation function, measured by the nmr technique is contrasted with the radioactive tracer diffusion and other techniques. The relevance of correlation function method is emphasised. Such a method leads to the problem of various molecular models and the various estimates of the molecular parameters. Under these premises other workers' study of the liquid state is reviewed. The nature of an Arrheniuslike equation is discussed. With these in view, the purpose of the work described in this Thesis has been to study the molecular motion of small, simple molecules with fairly simple intermolecular potential and a few possibilities in internal mobility in neat phase, along their liquid-vapour co-existence curve. Such a study would give us an idea about how far the belief, that even the motion of non-symmetrical molecules is inertial and coherent, is true. The other purpose

has been to chart the various rotational and translational
courses of the molecules in the high temperature region, namely
from room temperature to say about 80 $^{\circ}C$ below the critical
temperature. The effect of translation-rotation coupling and
the influence of the molecular shape, size and dipole moment
on the molecular motion is looked into. The self-diffusion
coefficient and the coefficient of viscosity with their inter-
relationships are especially looked into to discern the stamp
of micro motions on them. The prevalent belief that a hard
sphere model for the molecules is good enough to explain most
of the experimental findings in the liquid state of matter is
tested in the Appendix. Also discussed in the appendix are
the various approaches to estimate the self-diffusion coefficients
in molecular liquids, χ parameter to test for the type of motion
(diffusional and inertial) and the translation-rotation coupling
are discussed there.

Chapter 2 consists of the description of the experimental
set up for the measurement of fluorine ($Z=19$) and proton ($Z=1$)
spin-lattice relaxation times and molecular self-diffusion
coefficients in various compounds as a function of temperature
by pulsed nmr technique. The salient features of the home-made
9.8 MHz pulsed nmr spectrometer and the experimental methods of
data collection and the required parameter evaluation are given
in this chapter. The scope and limitations of the spectrometer,
tuning of the spectrometer, test sample run, reproducibility,

and limit of error in the experimental data are discussed. The bulk of T_1 and D data thus obtained could be of help in understanding molecular liquids.

With a view to analyse data later, Chapter 3 is devoted to the theoretical aspects of rotational motions. It has been an observed fact that the translational motion of the molecules is most likely diffusional, $i.e.$ the motion consists of short random steps. The rotational motions have been found to be highly characteristic of the molecules. Hence a detailed discussion of the diffusional (surrounding limited) and inertial (free) motions is given. In case of the coherent reorientational motion the angular velocity autocorrelation time varies directly as the square root of temperature. The surrounding dependent diffusive motion is strongly temperature dependent.

Chapters 4 and 5 contain respectively both data and analyses of results in simple molecules containing the methyl (CH_3) group, $viz.$ CH_3I CH_3CN, CH_3NO_2 , CH_3COCH_3, CH_3SOCH_3 and some assorted molecules such as CH_2Cl_2 , CH_2I_2 , anisole ($C_6H_5OCH_3$), and α-trifluoro toluene ($C_6H_5CF_3$).

The basic feature of the simple methyl group compounds except dimethyl sulfoxide studied in Chapter 4 is the slow variation of the spin-lattice relaxation time with temperature. In all except CH_3SOCH_3 the reorientational motion is characterised

by the inertial nature. The good deal of reorientational coherence in CH_3NO_2 does not seem to be getting affected by the large dipole moments of the molecules of such a highly polar liquid. The reorientational motion in CH_3SOCH_3 is diffusive in nature. In the molecular dynamics of CH_3SOCH_3 there seems to be a strong translation-rotation coupling. Liquid CH_2Cl_2 and CH_2I_2 although belong to the same family of halogen derivatives and though are structurally similar, the reorientational process in the former is inertial, whereas that in the later is diffusional. In addition to this, CH_2I_2 also shows fairly strong translation-rotation coupling and that the motion about the parallel symmetry axis of CH_2Cl_2 is somewhere between inertial and diffusional limits — but close to the diffusion end. Anisole and α-trifluoro toluene have mobile groups within the molecules. A simple analysis of anisole data leads to the observation of a correlation time characteristic of a free motion which might arise due to the intramolecular CH_3 group rotation. In α-trifluoro toluene the ^{19}F relaxation shows large, highly temperature sensitive spin-rotation interaction which seemingly arises because of the CF_3 rotation, and seems to be temperature activated. [1]H intramolecular interaction is modulated by the overall diffusive reorientation of the $C_6H_5CF_3$ molecule.

In the concluding chapter (Chap. 6) a summary of the work presented in this thesis is given and it is felt that molecular liquids will be better understood combining all the ancillary experimental data.

The Walrus said, "Let us talk of many things ...

CHAPTER 1

INTRODUCTION

Of all the branches of magnetic resonance nuclear
magnetic resonance has come a long way in looking ably into the
static and dynamic behaviour of molecules in matter. It has a
special place of pride so far as the dynamical studies in fluids
are concerned. Liquids, the awkward in-between of the solid and
gas phases (Powles (1974)), have proven difficult for comprehen-
sion. With the success achieved in understanding atomic liquids
molecular liquids are gradually engaging the attention of the
investigators. NMR has established itself as a good experimental
tool in the study of molecular liquids.

The microscopic study of matter often boils down in
practice to the study of their constituents: molecules and
atoms. So far as molecular physics is concerned the research
interest falls into two distinct categories. First, the
study of the static properties of the molecules, arising
because of the charge distribution within, gives an idea about
the molecule *per se.*. Chemical and biological scientists exult
in such information. Second, the study of the dynamic propert-
ies of the molecules lets us know how they behave as a commu-
nity with mutual interactions. This is of immense interest
to those who wish to know about the molecular dynamics

in that state of matter, matter in various phases of existence
and the like. The subject of our study is a part of the
second.

The study of liquids from the time of van der Waals to
the present has given workers in this field a very hard time.
Liquids are neither as orderly as solids nor as random as gases.
There exists only a short range order.

In the study of molecular dynamics two important aspects
come to the fore.   First, the molecule moves as a whole body
translating, rotating, reorientating. Second, there are
inner convulsions within the molecule where the various parts
which make the molecule, can sometimes rotate relative to one
another, reorientate or get exchanged with the surrounding.
If the whole and the segmental motions are responsive to each
other because of the coupling between them, the dynamical study
becomes complicated and more challenging. NMR rises to the
occasion in exploring into molecular motion in fluids and
particularly scores high so far as its contribution to the
understanding of molecular rotation is concerned. Although
nmr times and molecular motion characteristic times are vastly
different (10^{-8}s vs 10^{-12}s)   the systematics of temperature
and pressure variations of nmr parameters have enabled one
to make models and infer about the dynamics.

I.1   Basic Principle

A collection of nuclear spins each of spin I in a zero external magnetic field has all its $(2I+1)$ levels equally populated. When an external magnetic field H_0 is applied the Zeeman type interaction given by

$$E = - \underset{\sim}{\mu} \cdot \underset{\sim}{H}_0 \ , \qquad (1.1)$$

(where E is the energy of the magnetic dipole of moment $\underset{\sim}{\mu}$) lifts the degeneracy of the system. The spins interacting with the other degrees of freedom, called the lattice or reservoir, will tend to come to thermal equilibrium with the lattice. As the lattice is taken as a classical system the population distribution in the various nondegenerate levels will be governed by the Boltzmann statistics. The rate at which a net macroscopic Magnetization $M_0 = \chi_0 H_0$ (where χ_0 is the bulk static susceptibility) is established is called the spin-lattice relaxation rate. The rate at which the coherence existing between the spins is lost, $i.e.$ the rate at which the spin system in bulk matter attains thermal equilibrium within itself is called the spin-spin relaxation rate. Such relaxations in bulk matter are given by the Bloch's phenomenological equation (see Abragam (1961)),

$$\frac{d\underset{\sim}{M}}{dt} = \gamma (\underset{\sim}{M} \times \underset{\sim}{H}) - \hat{\imath}\, \frac{M_x}{T_2} - \hat{\jmath}\, \frac{M_y}{T_2} - \hat{k}\, \frac{M_z - M_0}{T_1} \ , (1.2)$$

where γ is the gyromagnetic ratio of the nucleus under consideration and M_x, M_y, M_z are the components of the bulk

magnetization $\underset{\sim}{M}$, and the magnetic field $\underset{\sim}{H}$ is set along the z-direction. In solids the spins are coupled more tightly to each other than to the lattice, which makes the spin-spin relaxation times much shorter than the spin-lattice relaxation times. Thus, spins in solids are said to have a spin temperature distinct from the lattice temperature and also the system is visualized as one with many degrees of freedom. In liquids the spin-spin interaction is quite weak and is of the same magnitude of strength as the spin-lattice interaction. Therefore it is assumed that the nuclei in a molecule (and some time groups of nuclei too) see the lattice independently of other spins or group(s) of spins. Both the relaxation times are of the same order of magnitude unless special cases like quadrupolar interactions, exchange of the resonating nuclei between nonequivalent sites, coupling to a quadrupolar nucleus and presence of paramagnetic nuclei occur. Due to the rapid molecular motions in liquids the local fields which are an index of the strength of interaction experienced by the nuclear spin get very much weakened leading to the observed narrow resonance line widths: in the magnetic field equivalent, of the order of a fraction of a milligauss. This motional narrowing coupled with the relative heavyness of the nuclei enable us to express in classical terms the very cumbersome quantum mechanical expressions for the molecular motions in a liquid. The density matrix (Wangsness and Bloch (1953), Redfield (1965) and the linear response methods

(Kubo (1957a, 1957b, 1966), Deutch and Oppenheim (1968),
Kivelson and Ogan (1974)) are most suitable for this purpose.
In the case of weak coupling of the nuclear spin to the lattice
although both the methods give the same result, the density
matrix method is more conventionally used. Further, this method
obviates the consideration of the limitations of the phenomeno-
logical Bloch equation which is valid in liquids because of a
number of generally realizable conditions. The molecular motions
do not produce any shifts in the energy levels of the spin system
but they affect relaxation mechanisms.

Molecular motions in liquids can be of two extreme kinds:
The diffusional motions are attributes of asymmetric large
molecules. Here, the molecular motion greatly depends on the
forces and torques exerted by the surrounding molecules. There-
fore in such asymmetric molecular liquids it is natural to expect
the viscosity parameter to be a good indicator of molecular
dynamics. In small spherical molecules the intermolecular forces
and torques will be of less consequence as the potentials are
expected to be small, symmetric. The molecular motion then is
more or less oblivious of the surroundings, and the molecular
inertial parameters, *viz.* mass and moment of inertia, chiefly
determine the translational and rotational motions and
therefore such characteristic motions are called inertial. The
wide variety of molecular symmetry and inertia ensures a spectrum o

possibilities between these two extreme models. Cases of isotropic and anisotropic motion arise depending on whether the motions of and about the molecular axes are similar or otherwise. Sometimes one could expect the motion of a molecule as a whole to be diffusional but the motion of its segment(s) to be inertial. A case to the point is the overall diffusive motion of biggish organic molecules and the facile motion of the segmental $-CH_3$ group which is quite free or inertial. The internal rotational motions can be of various kinds as described in the following: 1. In the 'Free Rotation' kind the internal rotation is free or inertial. 2. In the 'Rotational Diffusive' kind the internal motion is such that a vector fixed to the internal group changes in small angular steps. 3. When the rotational motion of such a vector takes place in large angular steps with fixed molecular orientation between jumps, such motions are called 'Jump Diffusive'. 4. Random large angle jumps in angular position with free rotation during the time between them entails the name 'Free Diffusive'.

The microdynamic behaviour of liquid molecules, namely their translation and rotation, leave their signatures on the measurable 'dynamic' parameters like the relaxation times and self-diffusion coefficients. It has been an interesting exercise theoretically to relate the micromotions to macroparameters and infer about the molecular dynamics from the observed macroparameters in liquids. (See Powles (1966), Waugh (1966), Hertz (1967), Zeidler (1971a) and Jonas (1973).) Gordon (1968) shows

how the correlation functions can be related to the micro-
dynamics and how the correlation functions can be extracted
from the Fourier transformation of the various spectroscopically
observed **macroparameters**. The mathematical ground work
required for a quantitative appreciation is given below which
shows how the spin relaxation measurements and self-diffusion
coefficients can convey some information about molecular motion.

In liquids, because of the rapid molecular motion the
spins are very weakly coupled to the lattice. Such a time-
dependent coupling can be given by a Hamiltonian

$$H_1(t) = \sum_{q=-2}^{2} (-1)^q F^q(t) A^{-q} , \qquad (1.3)$$

where $F^q(t)$ is the lattice operator, a stationary random func-
tion of time which carries the molecular time development
information; A^q is the space-quantized spin operator. The
irreducible operators F^q and A^q transform exactly like the
spherical harmonics. The contribution of an interaction of the
type cited above to the spin-lattice relaxation rate is

$$1/T_1 \propto J(\omega) = \int_0^\infty e^{-i\omega\tau} G(\tau) \, d\tau , \qquad (1.4)$$

where $G(\tau)$, the correlation function of the lattice parameters,
is given by

$$
\begin{aligned}
G(\tau) &= \sum_q G_q(\tau) \\
&= \sum_q \langle F^{q*}(t) \, F^q(t+\tau) \rangle_{av} \\
&= \sum_q \langle F^{q*}(0) \, F^q(\tau) \rangle_{av} , \qquad (1.5)
\end{aligned}
$$

with $<...>_{av}$ standing for the ensemble average, and $J(\omega)$ is the spectral density at angular frequency ω. For a stationary process the decay of the correlation function is given by an exponential relation with characteristic time τ_c, the correlation time for the analogous fluctuation (molecular motion) under consideration, such as

$$<F^{q*}(0) \; F^q(\tau)>_{av} = <|F^q(0)|^2>_{av} \; e^{-|\tau|/\tau_c}. \quad (1.6)$$

Hence the relaxation rate for such a motion would be

$$1/T_1 \simeq \Sigma <|F^q(0)|^2>_{av} \; \tau_c/(1+\omega^2\tau_c^2) \; . \quad (1.7)$$

In the present studies of molecular dynamics we have to simply pin-point the fluctuations contributing to relaxation and then try writing down the lattice and spin functions. All except τ_c in the foregoing equation being known, it is a small step further to have a glimpse of the characteristic time of the fluctuation under consideration. One great simplification in the calculation of τ_c occurs as the molecular motional processes are extremely rapid (the motional characteristic times are of the order of 10^{-11} to 10^{-14}s) thus making for nmr experiments $\omega\tau_c<<1$ (as the usual working frequency ranges from 1 to 300 MHz). This, popularly known as extreme narrowing condition, gives

$$1/T_1 \propto J(0) = \Sigma <|F^q(0)|^2>_{av}\tau_c \;,$$

or
$$\tau_c = \int_0^\infty \sum_q <F^{q*}(0)F^q(\tau)>_{av}d\tau / \sum_q <|F^q(0)|^2>_{av}. \quad (1.8)$$

The integral on the right hand side shows that the correlation
time is related to the area enclosed by the correlation function
but not to the actual shape of the correlation function. Light
scattering and infrared methods (Gordon (1968) Berne and Pecora
(1976)) give information about the correlation function *per se*.
The correlation function obtained from such experiments
integrated appropriately (Steele (1963a,1963b))can serve as a
check on the nmr results. Further, the importance of the
integrals of the correlation functions is no less in that they
can also be related to appropriate macroscopic transport
coefficients (see Chester (1963), Zwanzig (1965), Kubo (1966),
Eglestaff (1967) and Steele (1969)). A frequency dependent
relaxation rate measurement(Noack (1971))can surely provide
more information about the molecular dynamics.

The same kind of molecular motion can simultaneously modulate
several interactions leading to spin relaxation. With each
kind of the motion a characteristic motional correlation time
is associated. Therefore the analysis of the various relaxation
rates leads to the determination of the motional correlation
times.

The translational correlation time is a measure of the
persistence of the translational motion. It is natural to expect

the self-diffusion coefficient and intermolecular dipolar interaction, which are predominantly intermolecular spin separation dependent, to be governed by translational correlation time τ_t.

The persistence of molecular orientation in the laboratory frame will be a measure of the reorientational correlation time τ_θ. It is natural to expect a relation between τ_θ and rotational diffusion coefficient ($\mathcal{D}_{rot}$). Since an intramolecular dipolar vector, because of the molecular motion, can have different orientations relative to an external magnetic field, the intramolecular dipolar relaxation rate can give an idea of τ_θ. In the case of the quadrupolar nuclei the relaxation is due to the strong coupling between the quadrupole moment and the intramolecular field gradient. Molecular tumbling (i.e. orientational changes) modulates this interaction and hence a study of the quadrupolar relaxation rate could finally lead to a knowledge of τ_θ. The chemical shielding at a resonating nucleus arises because of the bilinear coupling between the resonating spin and the external field through the surrounding molecular electrons. If the coupling is isotropic the chemical shift or equivalently the local magnetic field is not modulated by the molecular orientation. However anisotropic chemical shift leads to a fluctuation of the local field at the resonating spin and therefore to spin relaxation. Thus an estimate of the contribution of anisotropic chemical shift to relaxation can also give information about τ_θ.

The characteristic time for angular momentum correlation τ_J is a very important parameter. A *priori*, the persistence of the rotational motion τ_J is expected to be determined by the molecular moment of inertia and the intermolecular frictional torques. Along with the molecular rotation, the molecular electrons too rotate and give rise to a local magnetic field at the resonating spin persisting as long. The local field fluctuates with the fluctuation of the molecular rotation. The coupling between this fluctuating local field and the resonating spin is responsible for the spin-rotation relaxation. The determination of the spin-rotation relaxation rate would thus lead to τ_J evaluation.

The molecular free rotational correlation time (τ_{free}), determined by the thermal kinetic energy and the moment of inertia is another rotational parameter useful for understanding the dynamics.

A nuclear spin type under observation, if migrating from one molecular site to another gives rise to a small residence time at a site which suitably modulates the nmr relaxation **rate. The** rate studies can therefore yield such average residence times. Sometimes the resonating nuclear spins, though static in a molecule, if coupled to an exchanging spin or a fast relaxing spin bear the mark of the **prevalent** process. Rotating frame experiments (Farrar and Becker (1971)) proved convenient to determine such 'exchange correlation times' τ_e.

Although τ_θ and τ_J are the characteristic times related to the general rotational motion of the molecule they must be properly differentiated. The molecular collisions set in torques which affect the molecular rotation. Therefore it is the molecular collisions which determine τ_J. In a classical rotational random walk having short free rotations interrupted by hard collisions (the diffusion limit) short τ_Js are found. The average angle of rotation $\bar{\theta}$ if short, many random walk steps will then be necessary for a sizeable orientational change (say by 1 radian) and therefore τ_θ is much longer than τ_J. This is the diffusion limit. For small, symmetric molecules the angular velocity is quite large and therefore $\bar{\theta}$ is large during τ_J and hence $\tau_\theta \sim \tau_J$. This is the inertial situation. In the free gas situation the collisions are few and far between, although during the interval between collisions there may be sizeable orientational change thus making $\tau_J > \tau_\theta$. The relative values of τ_J and τ_θ and the systematics of their variation with external constraints like temperature and pressure would yield a picture about the molecular dynamics. In the following the relationships between the correlation times, relaxation rates and self-diffusion coefficient is discussed.

The self-diffusion coefficient is a measure of the linear velocity autocorrelation. The characteristic time of the linear velocity autocorrelation is directly related to the self-diffusion coefficient. The Bloembergen, Purcell and Pound (1948) correlation function approach for a spherical body of radius 'a' finally

leads to the relation

$$\tau_t = 2a^2/\mathcal{D} , \qquad\qquad (1.9)$$

where τ_t is the translational correlation time, and $\mathcal{D}$ the self-
diffusion coefficient. As the self-diffusion coefficient and
the intermolecular dipolar interaction arise because of the
translational motion of the molecules, it has been gainfully
shown by Torrey (1953) that in the random flight model of the
molecules undergoing isotropic translational diffusion, in the
limit of small mean squared flight paths and small times
between the jumps,

$$(1/T_1)_{inter} = \pi\gamma^4\hbar^2 N_A n\rho/(5M_r a\mathcal{D}), \qquad (1.10)$$

where $(1/T_1)_{inter}$ is the intermolecular dipolar contribution
to the relaxation rate, n is the number of resonating spins per
molecule, N_A is the Avogadro number, ρ is the density of the
liquid sample under consideration, M_r is the molecular weight
of the compound under study, and a is the average hard sphere
radius. This result has the explicit assumption that the
resonating spin is situated at the centre of the molecule.
Hubbard (1963a), however, estimated that the consideration of
off-centre resonating spins increases the relaxation rate
estimation by only about 6%. Torrey's derivation also did not
take into account the radial distribution function of the liquid.
Consideration of the radial distribution function will increase
the intermolecular relaxation rate estimation. The experimental
method for estimating the intermolecular relaxation rate is
through the dilution study in the perdeuterated analogue of the
compound. The concentration dependent relaxation rate of the

substance in solution with its perdeuterated analogue is extrapolated to zero concentration to give the intramolecular relaxation rate (see for example, Bonera, Rigamonti (1965), Powles and Figgins (1965, 1967), Gillen, Schwartz and Noggle (1971)). Subtracting the intramolecular relaxation rate from the total relaxation rate of the normal substance gives the intermolecular relaxation rate. This method though very elaborate and accurate, is very often thwarted by the non-availability of the perdeuterated analogue compounds. However, Torrey's formula even without the inclusion of the purported corrections gives very good intermolecular relaxation rate estimates. Works which have also corroborated such a feeling are by Mitchell and Eisner (1960), Eisner and Mitchell (1961), Moniz, Steele and Dixon (1963), Powles and Figgins (1965), Muller (1966), Harmon and Muller (1969), Bull and Jonas (1970), Leblond et al (1971), Gillen et al (1971), Hwang and Freed (1975), Zeidler (1975), and Sandhu (1977). It is also realised that although a diffusion model predicts τ_t well the prediction of τ_θ from the viscosity (η) dependent Debye diffusion model,

$$\tau_\theta = 4\pi\eta a^3/3kT , \qquad (1.11)$$

is many a times quite erroneous.

The molecular radius needed to estimate the intermolecular relaxation rate is obtained using the Stokes-Einstein relation,

$$a = kT/6\pi\eta D, \qquad (.12)$$

where η is the coefficient of viscosity. The average molecular radius over the experimental temperature range is obtained using and η values. It is usually seen that, 'a' is about constant

over the experimental temperature range. Although the validity of such a relation for microscopic bodies moving in a surrounding of its own kind is suspect (Edwards (1970)), the good intermolecular relaxation rate estimates arising thereof somewhat justifies the means. It is shown in the appendix that the molecular radius estimated using the Stokes-Einstein relation happens to be of lowest magnitude compared to the Lennard-Jones radius, van der Waals radius and the hexagonal close packing radius of the molecule in the liquid phase. This being so, the use of any molecular radius other than the one derived by the Stokes-Einstein relation underestimates the intermolecular dipolar relaxation rate. Further, it is also shown in the appendix that when the hexagonal close packing radius estimates are used for calculating the relaxation rates, translational and rotational microviscosity factors (Gierer and Wirtz (1953)) must be used so that the relaxation rates are not underestimated. This consideration is automatically accounted for by the use of Stokes-Einstein radius estimates as shown in the appendix. Therefore, in the present estimation of the intermolecular dipolar relaxation rate a two step process is involved: in first showing the about constancy of $D\eta/T$ and calculating the average molecular radius therefrom; and then using the Torrey's relation to calculate the intermolecular dipolar relaxation rate.

Bloembergen, Purcell and Pound (1948) following Debye's method (Debye (1929)) for isotropic rotational diffusion of the dipole moment vector of the polar molecules, related the

intramolecular relaxation rate to the reorientational correlation time of a vector joining two resonating spins. The theoretical estimates for the intramolecular relaxation rate obtained thus are much larger than those experimentally observed. Such discrepancy could arise because of the inherent limitation of the Stokes-Einstein relation incorporated into the Bloembergen-Purcell-Pound model and also because of not taking into consideration the possibility of anisotropic rotational diffusive or inertial motion. Some other works towards a better understanding of the rotational process and the consequent relaxation are: (1) random walk model championed by Ivanov (1964); (2) rotational diffusion equation as advanced by Fury (1957), Favro (1960), Woessner (1962), Shimizu (1962), Huntress (1968, 1970); and (3) the rotational Langevin equation as followed by Hubbard (1963b), Steele (1963), and Atkins (1967). The Steele's inertial model takes into account large step, free rotational motion. The inertial model is viscosity independent and obviates need for consideration of the limitations of the Stokes-Einstein relation. The anisotropic rotational diffusion model advanced by Huntress (1968, 1970) is fairly detailed one and it obtains τ_θ for the various rotor types like asymmetric planar and symmetric top molecules etc.. For a two-spin system the relation between the intramolecular dipolar relaxation rate and the reorientational correlation time is given by (Abragam (1961)

$$(1/T_1) = 3\gamma^4\hbar^2\tau_\theta/2\hbar^6 , \qquad\qquad (1.13)$$

where $\hbar$ is the separation between the two resonating spins. One important thing to note here is that because of the $\hbar^{-6}$ dependence, spins other than the nearest neighbours will have negligibly small contribution to the relaxation rate and therefore in the analysis of the relaxation rate data one need only confine ones attention to the closest neighbours.

Significant spin-rotation contribution to ^{19}F relaxation in liquid $CHFCl_2$ were first reported by Gutowsky, Lawrenson and Shimomura (1961), and Brown, Gutowsky and Shimomura (1963). Later observations (Green and Powles (1965), Krynicki and Powles (1965), and Powles and Figgins (1965)) in small symmetric molecules too showed dominant spin-rotation contribution to proton relaxation even at high temperatures. A distinctive feature for the spin-rotation interaction is that with the increasing temperature the molecules retain higher angular momentum values longer and thus have longer τ_J. The persistence of the angular momentum for longer periods makes the spin-rotation relaxation rates larger. With the increasing temperature the translational and the orientational movements get faster and therefore the respective correlation times and the relaxation rates get smaller. Such an opposite temperature dependence of the spin-rotation relaxation is often of great help in separating the spin-rotation relaxation rate from the rest. (See, for example, Green and Powles (1965),

Powles and Figgins (1965).) The nmr has also the advantage over the molecular beam and microwave spectroscopy in giving small spin-rotation coupling constants in liquid state by non-destructive study of the experimental sample. Some salient relaxation expressions in the line of Huntress (1968) are as follows. In the diffusion limit ($\tau_J < \tau_\theta$, and therefore the rotational and reorientational motions are independent of each other), the rotational diffusion constant about the ith axis is related to the angular velocity autocorrelation time through the equation

$$D_i = (\tau_J)_i \, kT/I_i \, , \qquad (1.14)$$

where $(\tau_J)_i$ is the angular velocity autocorrelation time (also called the angular momentum correlation time) about the ith axis and I_i is the corresponding moment of inertia. In the principal co-ordinate system that diagonalizes the diffusion tensor

$$(1/T_1)_{SR} = 2/3\hbar^2 \, kT \sum_{i=x,y,z} [C_{ii}^2 - C_t(C_{ii} - C_t)] I_i \, (\tau_J)_i \, , \qquad (1.15)$$

where $C_t = 1/3 \, \mathrm{Tr} \, C$, C_{ii}s are the Cartesian components of the spin-rotation coupling tensor C, and the spin-rotation interaction hamiltonian is given by

$$H_{SR} = - \hbar \underset{\sim}{I} \cdot C \cdot \underset{\sim}{J} \, . \qquad (1.16)$$

Spin-rotation coupling constant calculation, *ab initio*, is difficult as it requires the knowledge of all the excited levels of the molecule. Since the spin-rotation and chemical shift

effects originate from the molecular electrons, they are mutually related (Flygare and Goodisman (1968), Deverell (1970) and such relationship are often of great help in the relaxation data analysis.

In case of isotropic rotational diffusion of a spherical body of radius a, the friction torque ξ is given by the usual Stokes-Einstein relation

$$\xi = 8\pi\eta a^3 .$$ (1.17)

However, in the inertial limit (Steele (1963)) the rotational diffusion and viscosity dependence notions are discarded in favour of a friction tensor whose diagonal elements, ξ_is , are related to the intermolecular potential through the relation

$$\xi_i = \frac{2I_i}{\pi} < \frac{\partial^2 V(\underset{\sim}{R}^N)}{\partial \psi_i^2} >$$ (1.18)

where $V(\underset{\sim}{R}^N)$ is the total intermolecular potential energy of N molecules in terms of $6N$-dimensional vector $\underset{\sim}{R}^N$ specifying the positions and the orientations, and ψ_i is the angle of orientation about the ith molecular axis and the angular momentum correlation time is defined by

$$(\tau_J)_i = I_i/\xi_i .$$ (1.19)

It is further shown that for an inertial (Gaussian) reorientation the minimum possible value of the reorientational

correlation time is given by

$$\tau_i = 1/2 (\pi I/3kT)^{1/2}. \qquad\qquad (1.20)$$

The diffusional and the inertial models are extreme ones and a realistic model for molecular motion in liquids however remains intractable. Chapter 3 deals with the spin-rotation interaction and the dynamically coherent reorientational motion in greater detail.

The chemical shift anisotropy relaxation rate and the quadrupolar relaxation rates have been stated to be directly related to the reorientational correlation time. Large chemical shift anisotropy is expected in cases where large diamagnetic shielding by the surrounding electrons occur. Further, the relaxation rate due to the chemical shift aniso-tropy varies as the square of the magnetic field strength. Since the present work is concerned with ^1H, ^{19}F relaxations which are known to have relatively low chemical shifts for any sizeable chemical shift anisotropy, and as low experimental magnetic fields are employed ($\sim 0.23T$) in the present work the chemical shift anisotropy is not a matter of concern as a relaxation agency. Whenever quadrupolar interactions are present as relaxation agents they are usually so strong that other interactions contributing to relaxation are negligible in comparison. The predominant quadrupolar relaxation rate makes the data analysis simpler. Quadrupolar nuclei are not of direct concern in the present work.

The coupling of a resonating spin to a fast relaxing quadrupolar nucleus has very little contribution to the observed total spin-lattice relaxation rate although it affects the spin-spin relaxation. The scalar coupling between the resonating spin I and the quadrupolar spin S finally leads to

$$(1/T_1)_{SC} = 2/3 \ A^2 S(S+1) \{\tau_S / [1+(\omega_I-\omega_S)^2 \tau_S^2]\} \ , \qquad (1.21)$$

and $(1/T_2)_{SC} = 1/3 \ A^2 S(S+1) \{\tau_S+\tau_S / [1+(\omega_I-\omega_S)^2 \tau_S^2]\} \ , \qquad (1.22)$

where $(1/T_1)_{SC}$ and $(1/T_2)_{SC}$ are respectively the scalar coupling contributions to spin-lattice and spin-spin relaxation rates; ω_I , ω_S are the Larmor frequencies of I and S spins respectively in the laboratory magnetic field and τ_S is the relaxation time of the nucleus S. The Larmor frequencies of ^1H and ^{19}F are so high that $(\omega_I-\omega_S)$ is usually several tens of magahertzes. Since τ_S is of the order of a few microseconds the quotient within the brackets of the right hand side of the equations (1.21 and 1.22) is small which gives $(1/T_1)_{SC} \sim 0$ and $(1/T_2)_{SC} \propto \tau_S$. Thus, in the spin-lattice relaxation data analysis of the present work the scalar coupling as a relaxation mechanism need not be considered.

Paramagnetic compounds have large magnetic moments. Even when they are present in the experimental liquid sample in small quantities their interaction with the resonating spin is so strong as to obliterate other relaxation mechanisms. It is imperative that the paramagnetic impurities are scrupulously removed from the experimental sample.

In molecules with more than two spins if all the spins
do not see dipolar interactions of the same strength, cross-
correlation between the various pairwise dipolar interactions
will result in a nonexponential relaxation process. Such cross-
correlations seem to strongly affect the intramolecular dipolar
relaxation, and an analogous spin relaxation nonexponential in
time; and the simple two spin Eq. (1.13) needs modification.
On the other hand the cross-correlation effects are small in
intermolecular interaction and Eq (1.10) is quite valid (see,
Hubbard (1958a, 1958b), Abragam (1961), Brooks *et al* (1968),
Hubbard (1969), Kitchlew and Nageswara Rao (1972a, 1972b, 1973a),
Cutnell *et al* (1975).

I.2   Some Salient Points on the Review of Others Work

The earliest approach to the study of molecular
dynamics was through hydrodynamics. The self-diffusion coeffi-
cient D was related to the coefficient of friction ζ through
the relation

$$D = kT/\zeta .$$
(1.23)

Stokes had earlier derived ζ for macrospherical body motion
in a liquid continuum. Einstein proposed the validity of the
Stokes relation for molecules moving in a crowd of their own
kind. Studies in molecular liquids in the line of Debye and
others showed the Stokes-Einstein relation to predict a smaller
diffusion coefficient than observed. Although the hydrodynamic
theory was too crude to be valid for the molecules

an attempt was made to retain it by using empirical correction factors in the equations for translational and rotational diffusion. It was pointed out that the (macro)viscosity coefficient when used for molecular motions needs lessening by the 'microviscosity factor', of magnitude greater than one. These corrected Stokes-Einstein relations were some what successful in predicting the translational and reorientational correlation times. In the case of solutions the 'mutual viscosity' concept of Andrade (Hill (1954, 1955)) based on the kinetic theory was successful. This theory had built in inertial parameter dependence and pre-eminent rotational features at low concentration. For monomeric liquids formed by small spherical molecules it was observed that the hydrodynamics idea of viscoous drag and stick must be discarded as the molecules are much freer to move about, oblivious of surrounding molecular attraction, than is a macrosolid body in a fluid. In the molecular motion there seems to be more 'slip' and less 'stick' than had been thought earlier. In this regard theoretical calculations à la Hu and Zwanzig (1974) and experimental studies by Bauer, Brauman and Pecora (1974) Bauer et al 1974 come to the fore. However, the primacy of a connection between the velocity autocorrelation and momentum transfer mechanisms of which statistical average measures respectively are the diffusion coefficient and shear viscosity coefficient, has always to be borne in mind in the mathematical constructs. The viscosity dependent spin-rotation relaxation study when extrapolated to zero viscosity if non-zero shows

the presence of internal motion (see, Bull, Barthel and Jonas (1971), Berne and Pecora (1976).

The diffusional (collision limited) process is *a priori* expected to be strongly temperature dependent. The inertial (free) motions on the other hand are quite oblivious of the surrounding and thus have a slow temperature dependence.

An useful method of testing whether the rotational microdynamics is diffusional or inertial is through the 'χ test'. (See, Bopp (1967), Wallach and Huntress (1969), and Gillen and Noggle (1970).) The ratio of the reorientational correlation time τ_θ to the free rotational time (τ_{free}) is given by χ. In the diffusion limit the small step collisions require much longer than the free rotational correlation time to change the molecular orientation sizeably - say by 1 radian. But in the inertial limit the orientational changes are through large steps and τ_θ , τ_J , τ_{free} being of the same order of magnitude, χ is usually found to be within 1 and 3. In terms of the intermolecular potential V, and the reorientational angle (ψ_i) about the molecular axis i, the χ parameter given by Huntress (1969) is,

$$\chi_i = \frac{5}{18} \sqrt{\frac{2}{\pi kT} \frac{\partial^2 V}{\partial \psi_i^2}} \qquad (1.23)$$

It is often that an anisotropic intermolecular potential is inferred from the observed diffusive nature of rotational motion.

A collisional efficiency parameter defined as the ratio of the rotational correlation time τ_J to the reorientational correlation time τ_θ tells how good a rotation changing collision is in changing the orientation of the molecule. As the rotational and reorientational changes go almost hand in hand in the inertial limit the collisional efficiency is unity. But in case of the diffusional motion, as many a collisions are necessary to give a sizeable net orientational change the collisional efficiency is very low. (See pertinent discussions on dense gases by Gordon, Armstrong and Tward (1968) and that on liquids by Maryott, Malmberg and Gillen (1974).)

The greater is the asymmetry of a molecule, the greater will be the energy transfer between rotational and translational motion. In order to monitor the molecular asymmetry, a translation-rotation coupling parameter κ introduced by McClung and Kivelson (1968), is given as the ratio of the intermolecular torque on the solute molecule to the intermolecular force on the solvent molecule. In terms of the intermolecular potential energy V, the κ parameter is given by

$$\kappa_{ii} \propto \frac{1}{a^2} \left(\frac{\partial^2 V}{\partial \phi_i^2} / \nabla^2 V \right) , \qquad (1.24)$$

where a is the mean radius of the molecule and ϕ_i is the angle of rotation about the molecular axis i. For spherical symmetric molecular potential, as does happen in spherical molecules, the

coupling is understandably zero. It was earlier thought that (Shimizu (1964), Wallach and Huntress (1969), Gillen and Noggle (1970)) large molecular dipole moments are responsible for the diffusive motion. The recent works of Bull and Jonas (1970), Assink and Jonas (1972), and Fury and Jonas (1976) show that it is the molecular shape which determines the extent of translation-rotation coupling. An interesting outcome of a good translation-rotation coupling is that the intermolecular and the intramolecular dipolar relaxation rates, which are dependent as the translational and reorientational motions respectively, will have similar temperature variation. Asymmetric molecules may be expected to show such a trend in their spin-lattice relaxation rates. As the asymmetric molecules will have to displace large volumes for orientational changes, pressure variation relaxation rate measurements will show large activation volumes. (See, McCall, Douglass and Anderson (1959), Bull and Jonas (1970).) The translation-rotation coupling has also been accounted for by bringing in a rough texture to the spheres of the hard sphere model (Chandler (1975)). Smooth spheres are germane to inertial motion. It is worthwhile pointing out that an implicit connection between the translation-rotation coupling and microviscosity idea exists. The molecular radius σ given by the relation **(1.11)**,

$$\tau_\theta = 4\pi\eta\sigma^3/3kT , \qquad\qquad (1.11a)$$

is related to the hydrodynamic radius a given by the Eq (1.12),

through

$$\sigma^3 = \kappa \, a^3 \, , \qquad\qquad (1.25)$$

where $0 < \kappa < 1$. (σ and a can be viewed as rotational and translational radii respectively.) For most of the molecular liquids κ is seen to be between 0.1 and 0.3. From the foregoing relations (1.11a) and (1.25) κ is construed as one necessitated to retain the τ_θ - a relationship. In microviscosity parlance this end was achieved by reducing the macroviscosity coefficient (η) of the liquid by the microviscosity factor (see p. 40). Thus, an inverse relationship between κ and the microviscosity factor seems to exist. A recent work by Masood *et al* (1976) discusses anisotropic rotational motion and translation-rotation coupling in large polar molecules by an assorted relaxation studies.

The molecular volume and η dependence of the reorientational correlation time in the Debye model is an implicit result of the translation-rotation coupling. The greater is the molecular asymmetry, the greater will be the volume displaced as a molecule reorientates and η, which is an attribute of the translational motion in molecular physics, automatically determines the orientational motion. Sometimes (as in polar liquids), the good agreement of experimental results with the predictions from the Debye relation (Eq. 1.11) is highly misleading. It is shown by Cuckier and Lakatos-Lindenberg (1972), and Fung and McGaughy (1976) that two negative assumptions : (1) the Stokes law is

valid for microbody motion, and (2) the molecules even in highly polar liquids are monomeric; cancel each other in giving an apparently valid Debye picture. Therefore, in handling Debye relation due caution need be exercised.

The 'molecular dimension' in the liquid state has remained a very little understood parameter. The situation is complicated further by the molecular association, hydrogen bonding *etc..* In gases the van der Waals idea and analogous Lennard-Jones parameters are good means to an understanding of the molecular dimensions. In solids the lattice structure gives a firm standing to the molecules and hence to the intermolecular distances, molecular dimensions *etc..* But in liquids close neighbourliness and intermingling make it difficult to have a clear idea of the molecular dimension as the molecules, particularly nonspherical ones, can approach each other in a myriad of ways and inclinations. Sometimes the liquids are pictured with approximated spherical molecules hexagonally close packing the available volume. Although the various methods chosen for molecular dimension are of doubtful values, the one best suited for the work presented here is discussed in the appendix. (See comments by Abragam (1961) p. 326.)

It is also good to take note that the measured spin-echo nmr diffusion coefficients are single particle diffusion constants (Ahn, Jensen and Kivelson (1972)). The mutual diffusion constant through the tracer diffusion method Mills(1971)

claimed to be experimentally much more accurate than the nmr
method (because of experimental refinements incorporated over
the years) measures the concentration diffusion. However,
if only very small amount of tracer is present the tracer
diffusion and self-diffusion coefficients are identical.
Such diffusion values for copiously investigated samples like
benzene and water can be used as standard reference in diffu-
sion measurements. The pulsed nmr self-diffusion measurement is,
however, much superior to the methods of D estimation through
the relation between translational correlation time and
dubious value of molecular radius. (See, for example Bondi
(1968).)

There are two salient aspects of data handling. First,
the earlier classical frequency or energy domain work (the
Schrödinger picture) is fraught with spectral width problems
which arise mainly because of the experimental limitations.
Time domain work (the Heisenberg picture), is more suitable
where the time development of a physical system can be observed
directly and the information available is with less uncertainty
and noise. Nevertheless, Fourier transformation can take the
result obtained in one domain to the other. Pulsed nmr experi-
ment, which is pursued in the present work being a time domain
work, time development and time correlation of the physical
systems are directly and much more conveniently observed.
Second, the validity of the linear response theory of

irreversible thermodynamics plays a subtle but major role in the understanding of the molecular microdynamics through the observed macroparameters. Situations slightly away from equilibrium, as do happen in the motion at the microlevel, can be comprehended through the correlation functions which give an average picture over the observed time and space interval. Such integration or averaging does not erase all the information of micromotion. The characteristic time which is a measure of the microdynamic rate is carried through the integration process. As the integral of the correlation function is intimately related to the macroparameters the macro and the microparameters get connected. For example Oppenheim (1971) shows how two such parameters of present interest T_1 and D are related. Two things are to be clearly borne in mind. First, although the experimental time scale is longer than the molecular time scale (microseconds against picoseconds) one can still learn about the micromotion. Second, the molecular motional models have a relevance as long as the correlation functions are constructed first and then related to the macroparameter. The reverse approach namely the attempt to arrive at the validity of the models from macroparameters has very little significance. Models are necessary only so far as predicting the macroparameter is required. However, the systematics of the variation of macroparameters with external constraints like temperature and pressure reflect the character of the molecular dynamics.

1.3 Scope of the Present Work

The aim of the work presented in this thesis is to
get a picture of the molecular dynamics in the liquid-vapour
coexistence region of some molecular liquids through the *in situ*
measurement and analyses of T_1 and D data. The temperature
variation work in a liquid sample in a sealed tube has the
drawback that both the molecular kinetic energy and packing
(density of the sample) change with temperature variation which
are not accounted for in the data analysis. A better approach
could be the simultaneous pressure and temperature variation
study which could enable obtaining constant density T_1 and D
data which are more meaningful and better amenable to analyse
à la Jonas group of workers. The maximum vapour pressure built
on the experimental sample in the sample tube due to the tempera-
ture variation could be of the order of several tens of atmo-
spheres which is not much as to deviate T_1 and D from the normal
pressure values. The T_1 and D data are thus oblivious of the
large vapour pressures, but are affected by the large convection
currents in the sample.

A *priori*, the molecular shape, symmetry, mass, moment of
inertia, dipole moment *etc.* seem to affect the molecular dynamics
in liquid. The aim of such studies would be to ascertain the
extent of influence of such agencies on the molecular dynamics. The
two extreme kinds of molecular dynamics which ensue are diffu-
sive and inertial types. In the Brownian diffusion kind of the

translational, reorientational or rotational dynamics the
movement is collision limited, is through small steps, and is
severely surrounding dependent. The strongly surrounding
dependent dynamics reflects itself through a strong temperature
and viscosity dependence of the corresponding parameters. The
inertial kind of the dynamics is mostly determined by the
molecular mass and moment of inertia, and has very little
temperature and viscosity sensitivity. It is thus from the
temperature variation of the parameters related either to the
translational, reorientational, or the rotational motion the
nature of the concommitant dynamics be known. Since building
the microdynamic models from the microparameters are not defin-
itive ones (p. 47) observation of the trends of variation of
suitable parameters with temperature and pressure are very
helpful.

The molecular dimensions are closely related to the dynami-
cal parameters and there seems to be many approaches to deter-
mine such dimensions (see Appendix). In view of the nmr work and
its data analysis the Stokes-Einstein method of finding the
molecular radius from the experimental D, and η data seem to be
best suited. Such an approach seems to naturally account for
the microviscosity considerations and has important connection
with several other works as stated in the Appendix.

The self-diffusion coefficient is translational motion
dependent, collision limited and except in cases of highly

hydrogen bonded liquids like water, obeys an Arrheniuslike relation. The methods of estimation of the self-diffusion and rotational diffusion are also discussed in the Appendix.

In the asymmetric molecules the translation and orientational changes are well coupled as a collision would simultaneously and sizeably alter both. In such asymmetric molecules there will not be much scope for any reorientational coherence. Chapter 3 explores the outcome of the reorientational coherence as well as the diffusive process. The problem of the translation-rotation coupling is also touched on in the Appendix. An obvious outcome of the translation-rotation coupling is that the intermolecular relaxation rate and the intramolecular dipolar relaxation rate which depend respectively on the translational and reorientational motion vary similarly with temperature.

A coherent pulsed nmr spectrometer assembled for such temperature variation T_1, D work and other ancillary experimental arrangements are described in Chapter 2. The procedure for data gathering, the data credibility (error etc.) and the test sample runs are also described. For the periodical spectrometer checks it seems very helpful to make use of two test samples, water and benzene, copiously studied otherwise.

The dynamical parameters D and η combined variouly with ρ and T have often been used to analyse the molecular dynamics. Several other parameters like the free rotational period of the

molecule, reorientationl correlation time in the inertial
(Gaussian) limit, reorientational correlation time in the
diffusion limit, $a_2^m(0)$ defined by Steele and associates (Steele
(1963), and Moniz, Steele and Dixon (1963)), and the χ parameter
used to find the diffusion or inertial reorientation are also
helpful for studying the molecular dynamics. The intermolecular
relaxation, directly modulated by the translational motion, is
estimated by using the Torrey's relation. The intermolecular
relaxation rate separated from the observed relaxation rate
gives the intramolecular relaxation rate carrying information
about the orientational and rotational changes. As the orienta-
tional and rotational changes have opposite temperature dependence,
these can be separated in suitable cases from the temperature
variation work. In the event of absence of marked changes and
a minimum in the intramolecular relaxation rate such separation
is not possible. All these parameters are discussed in the
context of the studied molecules presented in Chapters 4 and 5.

The work presented in Chapter 4 particularly looks into
problem of molecular dynamics in some CH_3 containing liquids.
The CH_3 group is particularly quite facile about the bond to
the molecular skeleton. The large anisotropic rotational
symmetric tops like CH_3I and CH_3CN give rise to spin-rotation
interaction. In molecules like CH_3NO_2 and CH_3COCH_3 the barrier
to internal rotation is low and in the observed temperature
range inertial reorientations are seen. The large dipole moments

of CH_3NO_2 and the consequent possible local structure does not seem to affect the reorientational motion. In case of CH_3COCH_3 and CH_3SOCH_3 , the small barrier to internal rotation in the former gives rise to inertial orientational changes whereas the structural asymmetry in the later gives rise to a translation-rotation coupling.

The work presented in Chapter 5 deals with a group of assorted molecules. CH_2Cl_2 and CH_2I_2 belong to a family of halogen derivatives with CH_2I_2 more massive than CH_2Cl_2. Vestiges of inertial reorientations are seen in CH_2Cl_2 whereas the reorientational process in CH_2I_2 is diffusional. The liquid anisole has its molecules fairly asymmetric and with possibility of intramolecular rotation. The internal motion though not much prominent nevertheless makes itself felt in the analysis. The studies in α-trifluoro toluene suggests that the internal rotation mostly contributes to the ^{19}F relaxation which is spin-rotational in nature. The strong temperature dependence of the ^{19}F intramolecular relaxation, however, hints at a temperature activated process.

The summary and conclusion of the work presented here are given in Chapter 6.

CHAPTER 2

EXPERIMENTAL METHODS

Pulsed nmr method is suitable for investigation
of kinetic processes in the substances. The resonance
is non-adiabatically, transiently stimulated. The
observation of the re-establishment of the thermodynamic
equilibriums permits the separation of the static and
dynamic effects within the substances.

With an aim to study the molecular dynamics of
liquids over the liquid-vapour coexistence region by means
of the study of proton ($Z=1$) and fluorine ($Z=19$) relaxation
time and of the molecular self-diffusion coefficient, a
pulsed nmr spectrometer to work at a convenient radiofre-
quency (~ 9.78 MHz) is conceived. The method of spin echo
and the experimental arrangement is described in the
following.

2.1   Spin Echo

In the spin echo method (Hahn (1950)), one observes
the signals from the spin system when the excitation pulses
are off. This is a time domain experiment. This time
domain signal apart from being Fourier related to the
frequency domain continuous wave (cw) spectrum has several
advantages: (1) In contrast to the frequency domain signal

the time domain signals are easy to perceive. Direct analysis of the signals provides the relaxation times and the self-diffusion coefficients. (2) The excitation is off during the time the signal (echo) is observed. The observed signal, therefore, is free from the interference due to the excitation. (3) When the signal (echo) appears the receiving system is recovered from the excitation to normally receive the signal. (4) The same time domain signal from the repeated runs can be summed vectorially to average the non-periodic noise and give a better S/N. (5) The excitation and observation on the entire spin system is carried out in a time span much smaller than a cw experiment for the same amount of information (see Farrar and Becker (1971)) and therefore entails a good deal of time-saving.

To perceive the formation of the spin-echo let us first fix a set of Cartesian axes as follows. The static magnetic field direction defines the z axis of the static or laboratory frame of reference. The axis of the sample coil through which the rf excitation to the spin system is applied and which also record the subsequent response of the system; defines the x axis of the static reference frame. (See Fig. la.) A right handed system of Cartesian axes fixes the remaining axis y.
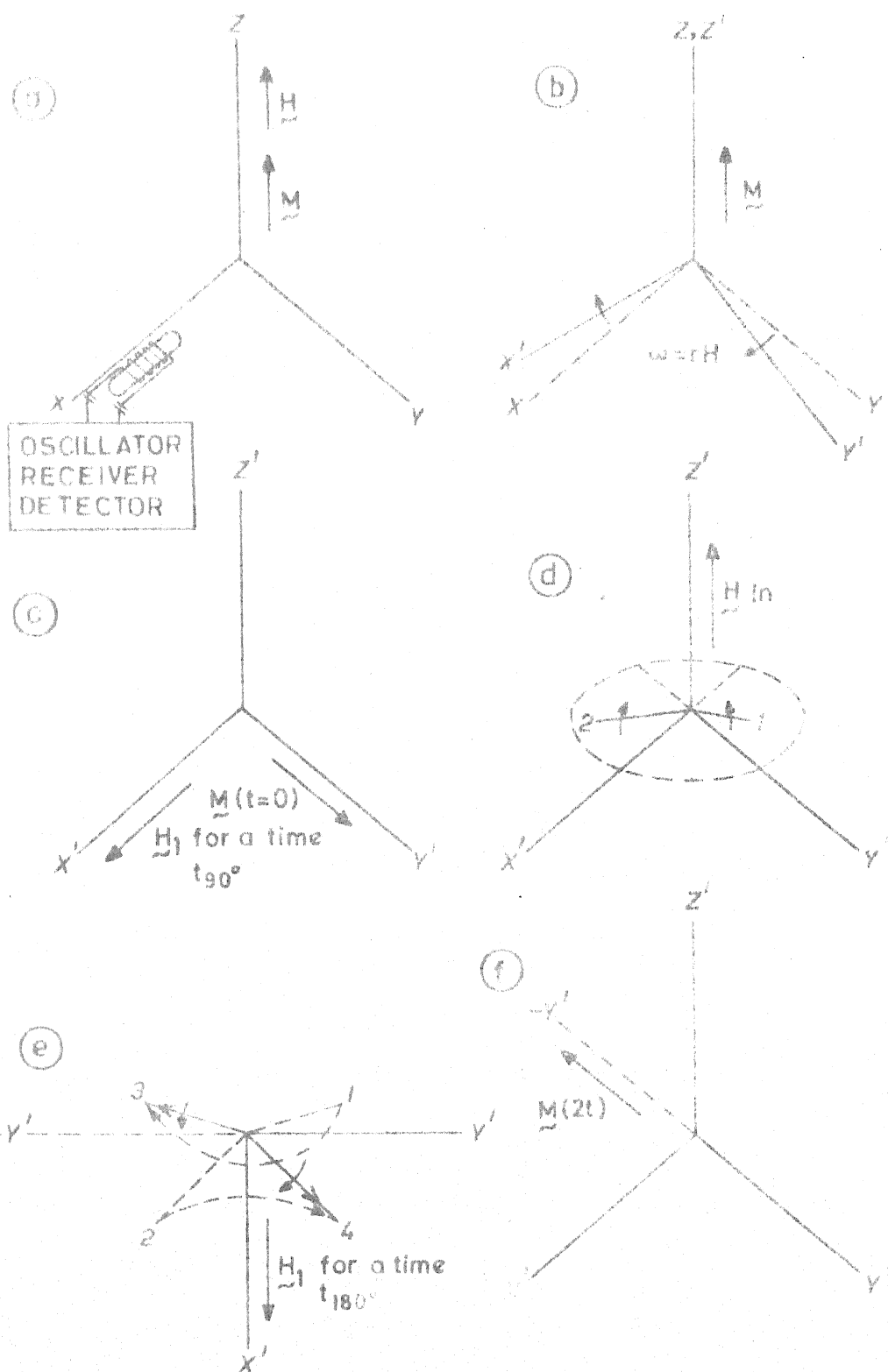
FIGURE 1. ECHO FORMATION WITH 90°-180° PULSE SEQUENCE

As mentioned in Chapter 1, a spin ($I=1/2$) system placed in a static magnetic field $\hat{k}H_0$ eventually in a time larger than the spin-lattice energy exchange time, attains thermal equilibrium (Boltzmann distribution of population amongst the Zeeman levels) amounting to a net magnetization along the static field. The dynamics of magnetic moment vector $\underset{\sim}{M}$ in a static homogeneus field $\underset{\sim}{H}_0$ can be given by (Abragam (1961))

$$\frac{d\underset{\sim}{M}}{dt} = \gamma(\underset{\sim}{M} \times \underset{\sim}{H}_0) .$$ (2.1)

In a frame rotating at an angular velocity $\underset{\sim}{\omega}$ the time derivative of the magnetization is given by

$$\left(\frac{d\underset{\sim}{M}}{dt}\right)_{rot} = \frac{d\underset{\sim}{M}}{dt} + \gamma(\underset{\sim}{M} \times \omega) ,$$ (2.2)

where the right hand terms in the expression are with respect to the static reference frame. Combining the Equations (2.1) and (2.2)

$$\left(\frac{d\underset{\sim}{M}}{dt}\right)_{rot} = \gamma\underset{\sim}{M}\left(\underset{\sim}{H}_0 + \frac{\omega}{\gamma}\right) .$$ (2.3)

The choice of $\underset{\sim}{\omega} = -\gamma\underset{\sim}{H}_0$ leaves $\underset{\sim}{M}$ static in the rotating frame (see eq (2.3), Fig.1b). The rotating frame has its Cartesian axis z' coincident with the static frame z axis but rotates about the z axis with the Larmor frequency $\omega = \gamma H_0$ in a sense apposite to $\underset{\sim}{H}_0$.

The presence of an rf field at the Larmor frequency
of the spin system under observation,

$$\underset{\sim}{H}_{rf} = 2\hat{\imath} H_1 \cos \omega t ,$$

can be resolved into two circularly polarized components
one of which is a counter-clockwise rotating field

$$\hat{\imath} H_1 \cos \omega t + \hat{\jmath} H_1 \sin \omega t ,$$

and the other a clockwise rotating field

$$\hat{\imath} H_1 \cos \omega t - \hat{\jmath} H_1 \sin \omega t ,$$

both of the same amplitude H_1. The clockwise rotating
field has the same sense of rotation as the previously
mentioned rotating frame of reference. In this clockwise
rotating frame the magnetization vector $\underset{\sim}{M}$ finds the field
$\underset{\sim}{H}_1$ static. Thus, in the rotating frame

$$(\frac{d\underset{\sim}{M}}{dt})_{rot} = \gamma (\underset{\sim}{M} \times \underset{\sim}{H}_1)_{rot} . \qquad (2.4)$$

This equation suggests that the rotation of magnetization
$\underset{\sim}{M}$ is about $(\underset{\sim}{H}_1)_{rot}$. If the rf is kept on for a time t_{90^0}
(a 90^0-pulse) such that $\gamma H_1 t_{90^0} = \pi/2$ the bulk magnetiza-
tion is brought along y' axis (Fig. 1c). Quantum mechani-
cally this situation corresponds to a superposition of the
two spin states. A 180^0-pulse of duration t_{180^0} (such
that $\gamma H_1 t_{180^0} = \pi$) tips the net magnetization along the

z axis to -z axis which in quantum mechanical parlance is equivalent to inversion of the population of spin levels. The duration of the pulses must be so short that the spins do not have enough time to exchange energy and behave separately from the collective bulk magnetization.

The rotating frame Cartesian axis x' is imagined to be fixed along the clockwise rotating H_1. In a coherent oscillator the oscillation being always present (even in absence of the pulses) the rotating frame x' axis may be imagined to be present always. A right handed Cartesian axis system defines the remaining y' axis. In such a system the 90^0-pulse tips the net magnetization to the y' axis. If the spins were free without interactions of any kind then they would stay coherently amongst themselves and therefore the bulk magnetization would stay put along y'. However, the interaction of the spins with the lattice leads to a thermal relaxation and growth of magnetization along $\underline{H}_0$. Further, the mutual spin-spin interaction leads to an irreversible loss of the coherence in a characteristic time T_2 and therefore an observed decay of the boulk magnetization in the transverse plane. For convenient observation of the net magnetization in the transverse plane at different times the decay of the magnetization is made reversible in the following ingenious way. In the presence of an inhomogeneous field $\hat{k}H_{in}(\bar{z})$, (Fig.1d),

where $H_{in}(z)$ is a function of the distance along the z axis, all the spins do not see the same field and therefore do not have the same Larmor period. As a result of this the isochromats (formed by the bunch of spin magnetizations seeing the same static magnetic field) fall apart from one another. The decay of spin coherence occurs in a character-istic time $1/\gamma H_{in}$, where H_{in} is the maximum inhomogeneous field over the sample. Ascertaining $1/\gamma H_{in} > T_2$ the present inhomogeneous decay is made much faster than the homogeneous decay. The important thing to note here is that at time $\tau < T_2$ although the isochromats may be fanned out and hence there may not be any transverse magnetization in the rotating frame, the memory of the inhomogeneous decay still persists in the isochromats. A second pulse at time τ (such that $T_2 > \tau > 1/\gamma H_{in}$) makes the isochromats regain their loss of relative phase due to inhomogeneous decay to come in phase (echo) at time τ further. This is easily visualized in case of a second, 180^0-pulse. The 180^0-pulse applied along x' satisfying the foregoing condition takes two of the representatives of the fanned out isochromats positioned at 1 and 2 to positions 3 and 4 (see Fig. 1e). These newly positioned isochromats retain their sense of rotation about z' axis. Therefore in a time τ further, except for the inhomogeneous spread, the isochromats will arrive in phase along $-y'$ (see Fig 1f). The decay of magnetization and clustering of the isochromats

z axis to -z axis which in quantum mechanical parlance is equivalent to inversion of the population of spin levels. The duration of the pulses must be so short that the spins do not have enough time to exchange energy and behave separately from the collective bulk magnetization.

The rotating frame Cartesian axis x' is imagined to be fixed along the clockwise rotating H_1. In a coherent oscillator the oscillation being always present (even in absence of the pulses) the rotating frame x' axis may be imagined to be present always. A right handed Cartesian axis system defines the remaining y' axis. In such a system the 90^0-pulse tips the net magnetization to the y' axis. If the spins were free without interactions of any kind then they would stay coherently amongst themselves and therefore the bulk magnetization would stay put along y'. However, the interaction of the spins with the lattice leads to a thermal relaxation and growth of magnetization along H_0. Further, the mutual spin-spin interaction leads to an irreversible loss of the coherence in a characteristic time T_2 and therefore an observed decay of the boulk magnetization in the transverse plane. For convenient observation of the net magnetization in the transverse plane at different times the decay of the magnetization is made reversible in the following ingenious way. In the presence of an inhomogeneous field $\hat{k}H_{in}(\bar{z})$, (Fig.1d),

where $H_{in}(z)$ is a function of the distance along the z axis,
all the spins do not see the same field and therefore do
not have the same Larmor period. As a result of this the
isochromats (formed by the bunch of spin magnetizations
seeing the same static magnetic field) fall apart from one
another. The decay of spin coherence occurs in a character-
istic time $1/\gamma H_{in}$, where H_{in} is the maximum inhomogeneous
field over the sample. Ascertaining $1/\gamma H_{in} > T_2$ the
present inhomogeneous decay is made much faster than the
homogeneous decay. The important thing to note here is
that at time $\tau < T_2$ although the isochromats may be fanned
out and hence there may not be any transverse magnetization
in the rotating frame, the memory of the inhomogeneous
decay still persists in the isochromats. A second pulse at
time τ (such that $T_2 > \tau > 1/\gamma H_{in}$) makes the isochromats
regain their loss of relative phase due to inhomogeneous
decay to come in phase (echo) at time τ further. This is
easily visualized in case of a second, 180^0-pulse. The
180^0-pulse applied along x' satisfying the foregoing
condition takes two of the representatives of the fanned
out isochromats positioned at 1 and 2 to positions 3 and 4
(see Fig. 1e). These newly positioned isochromats retain
their sense of rotation about z' axis. Therefore in a
time τ further, except for the inhomogeneous spread, the
isochromats will arrive in phase along $-y'$ (see Fig 1f).
The decay of magnetization and clustering of the isochromats

(echo) in the rotating frame induces signals in the labora-
tory sample coil modulated at the relative frequency of the
two frames. Ordinary amplitude detection of such signals
in the laboratory frame gives the free induction decay and the
spin echo. In a phase sensitive detection method, by properly
referencing the laboratory frame signal with respect to the
rotating frame (which, as mentioned earlier, is set by the
oscillations of the coherent oscillator) one can distinguish
between the sense of the decay of the y' magnetization and
the sense of the echo formed along $-y'$. The height of the
free induction decay after the 90°-pulsing of the equilibrium
magnetization, is a measure of that magnetization. The
echo formed at time 2τ from the first pulse is a measure of
the transverse magnetization remaining after the irreversible
loss for time 2τ and diffusion of spins during that time has
taken place. The echo height, therefore, carries information
about T_2 and $\mathcal{D}$.

Clark (1964), Farrar and Becker (1971) list elaborately
the requirements for a good spinecho spectrometer. The
salient conditions to be borne in mind are :

(1) $\gamma H_1 t_{90^{\circ}} = \pi/2$ and $\gamma H_1 t_{180^{\circ}} = \pi$.

(2) $t_{90^{\circ}}, t_{180^{\circ}} << T_1, T_2$.

(3) $t_{90^{\circ}}, t_{180^{\circ}} > \tau > 1/\gamma H_{in}$.

(4) $\tau > 1/\gamma H_{in} > t_{90^{\circ}}, t_{180^{\circ}}$.

(5) H_1 must be much larger than the range of the chemical
shift of the resonating spins so that all the spins
are tipped about H_1.

Work on liquids needs only a moderate amount of pulse power (Clark (1964), Farrar and Becker (1971)). Therefore pulse level of about 300 V delivered at an impedance of 50Ω suffices. Typical pulse widths are a few microseconds. The space available for the sample between the poles of the magnet is restricted because of the arrangement for heating and for temperature measurement, and by the coil required for exciting the sample under study. A single coil sample circuit is preferred as it requires less space and obviates the need for tuning arrangement. It also obviates the need for electrostatic shielding which would be required for a double coil (crossed coil) system. The nmr signal is directly amplified in an rf amplifier of band width 1 MHz tuned to 9.78 MHz which is just about the requirement in view of the pulse rise time and signal width (Mansfield and Powles (1963), Clark (1964)). The nmr signal which is essentially an audio modulation of the rf carrier is finally detected and retained for measurement on a storage oscilloscope screen. As the signals in the samples of our interest are quite strong no phase sensitive detection is incorporated. The resonant magnetic field is provided by a 12" pole diameter Varian magnet (Model VFR 2703) The self-diffusion in liquids being as high as $10^{-9} m^2 s^{-1}$ the use of a pulsed field gradient is unnecessary. A fresh dry cell gives the required steady, measurable field gradient. Figure 2 gives the block diagram of the experimental set up.
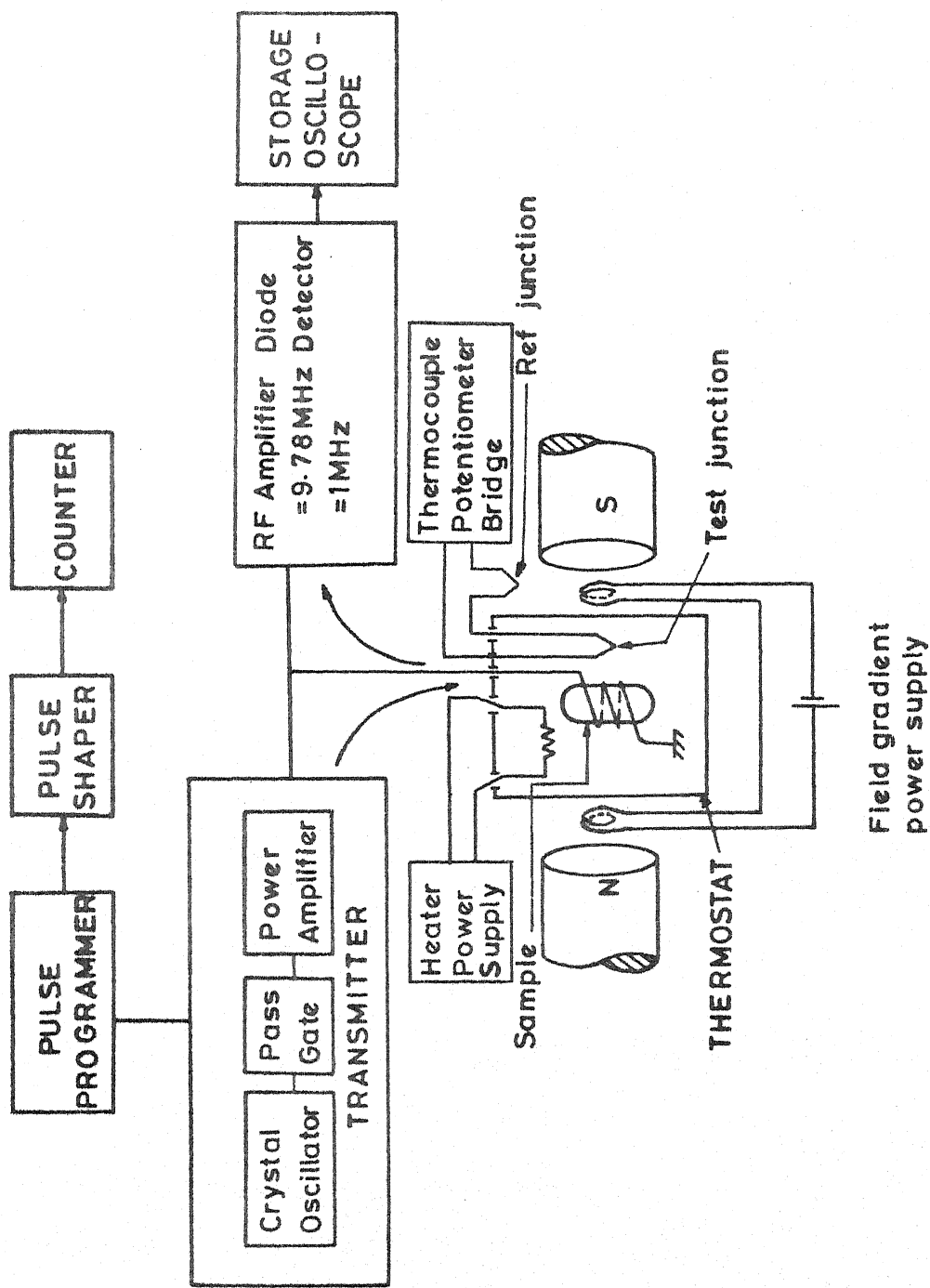
FIGURE 2. BLOCK DIAGRAM OF THE PULSED NMR ARRANGEMENT

2.2 Transmitter

Essentially Blume (1961)'s circuit for the transmitter
(Figure 3) followed also by Kitchlew (1971) is used in the
present work. The crystal oscillator works satisfactorily
without an oven. The pass gate consists of the low leakage
tube 7077 in order to give a very good carrier suppression.
This tube often gets soft after a prolonged period of work.
This is evidenced through a sizeable fraction of the rf carrier
leaking to the receiver and giving undesired phase detection.
Also then the plate cathode resistance is found to be low.
Another trouble arises from the 5093 transmitter power tubes
getting weak quickly. From time to time tuning of the coil-
condenser arrangement in the transmitter has been necessary in
order to maximise rf at the tank coil head (*i.e.* the sample head).
The transmitter is properly rf-shielded lest spurious ringing
and phase detected signals show up at the receiver output.

2.3 Pulse Programmer

The pulse programmer (Fig.4) consists of a number of
units from Tektronix 160 series and conventional pulse shaping
units for differentiation, inversion, mixing *etc.*. The detailed
schematic of the circuits is given in the Figures 5 and 6. The
programmer has the capability of giving one-, two-, or three-
pulse sequence in continuous or manual triggered mode. The
Carr-Purcell sequence can be had in the manual triggered mode
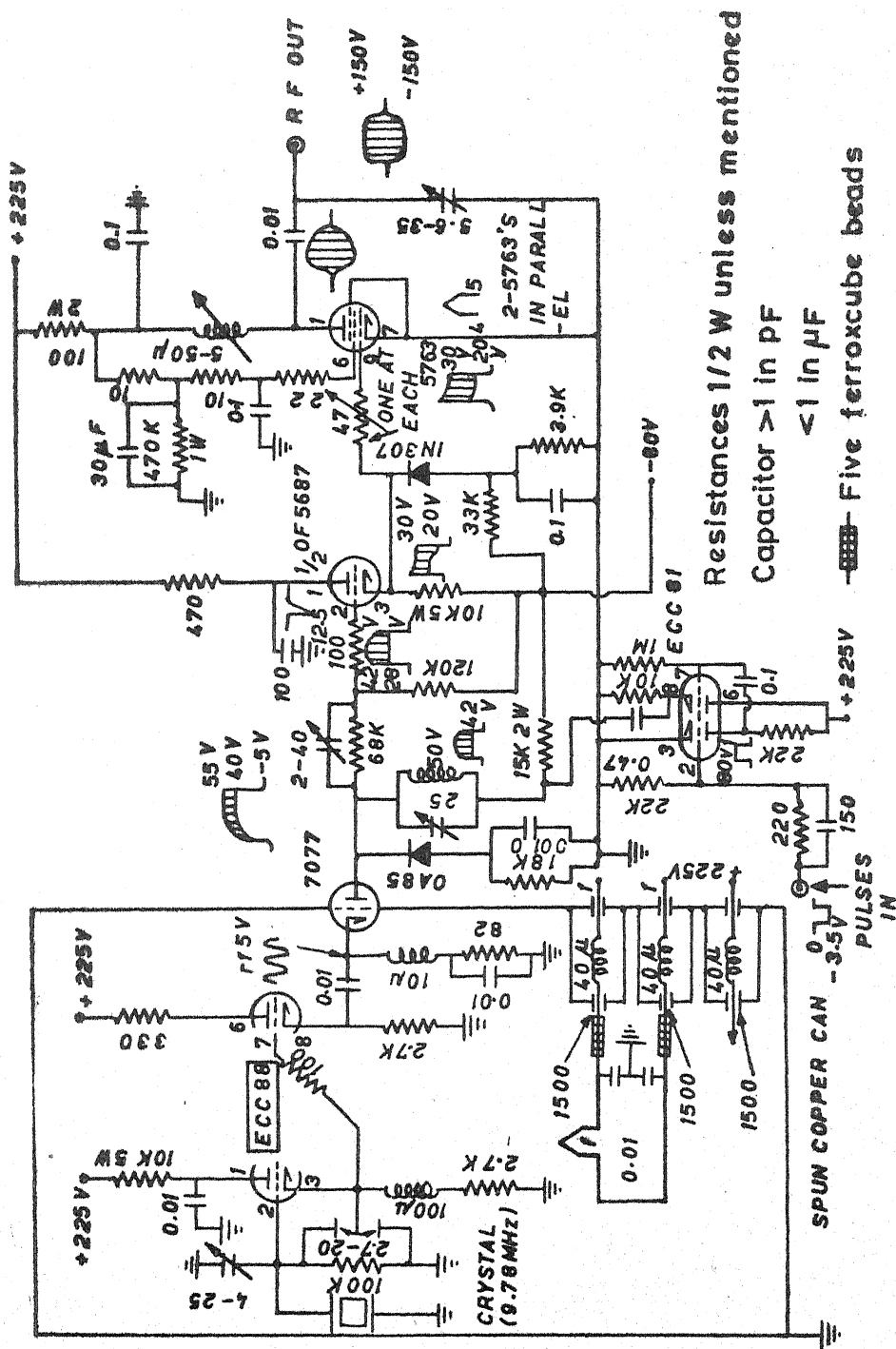
FIGURE 3. GATED OSCILLATOR

FIGURE 4. PULSE PROGRAMMER
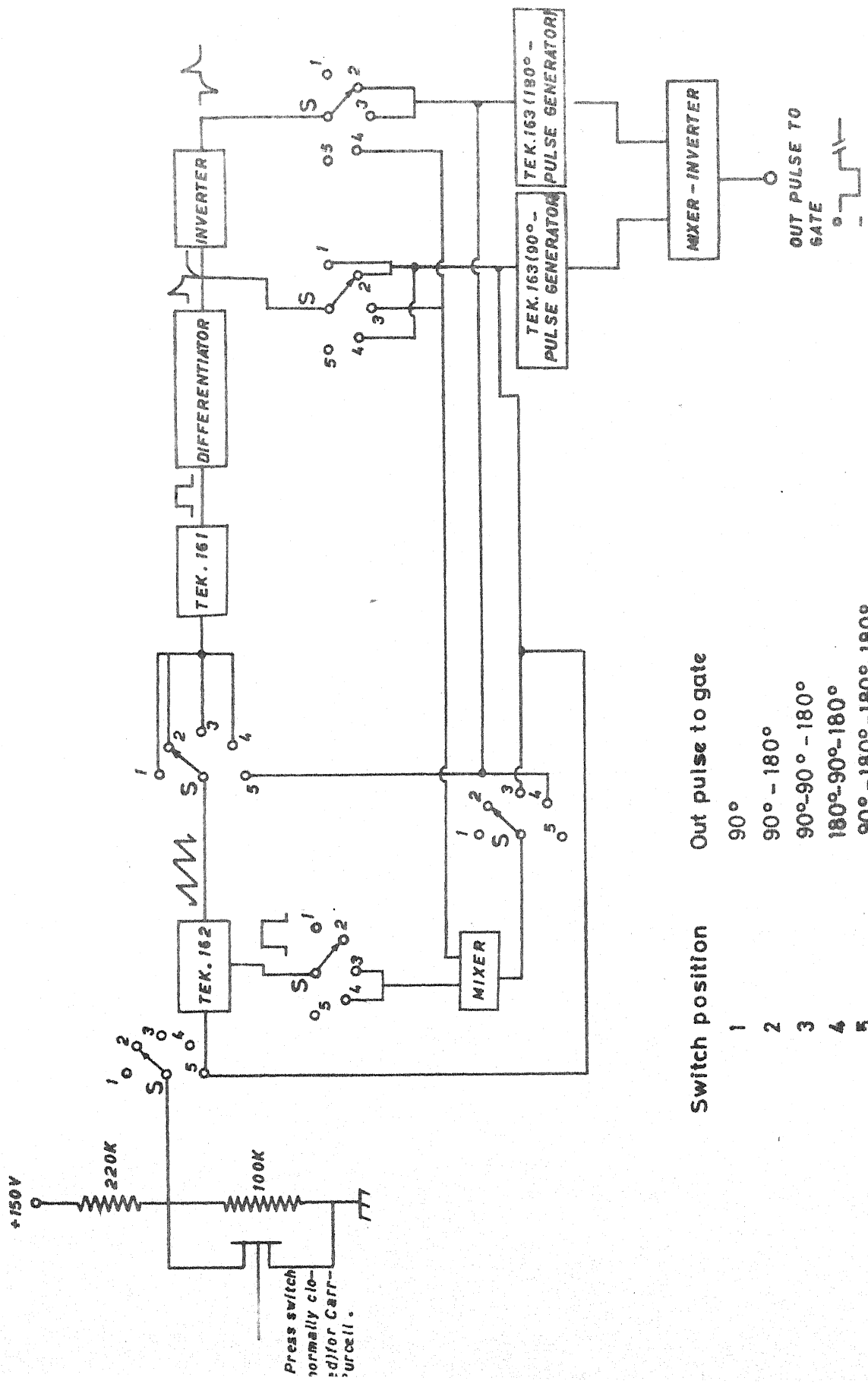
Switch position	Out pulse to gate
1	90°
2	90° – 180°
3	90°–90° – 180°
4	180°–90°–180°
5	90° –180°–180°–180° (CARR–PURCELL)
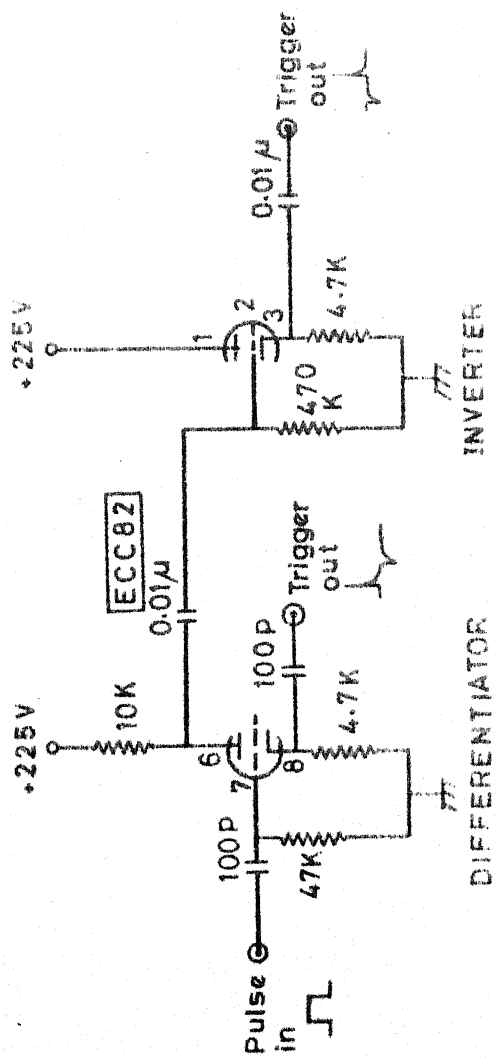
FIGURE 5. DIFFERENTIATOR - INVERTER
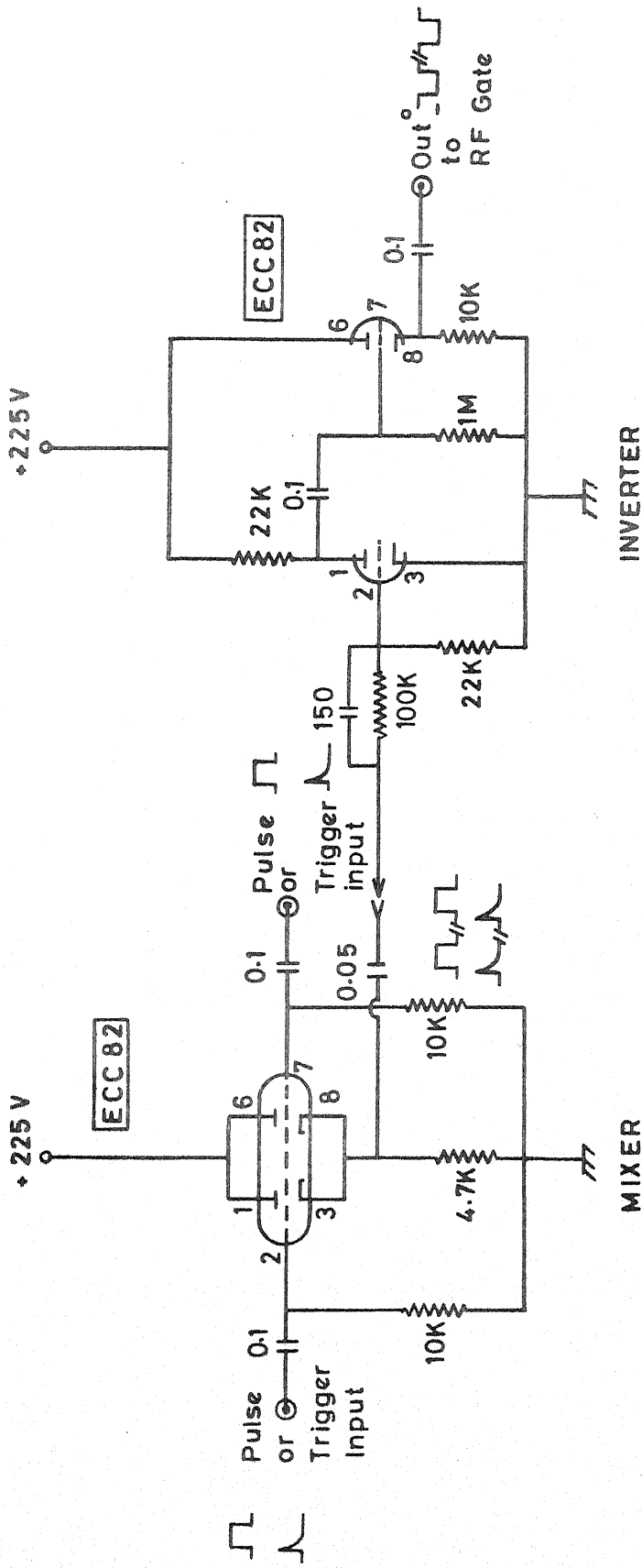
FIGURE 6. MIXER-INVERTER

only. (See for arrangement Figure 4 .) The programmed pulse
intervals are measured by an Hewlett-Packard counter (Model
521C) after passing through a pulse shaping unit (see **Figure 7**).

2.4   Receiver

The rf receiver has four stages of rf amplifier
stagger-tuned to a centre frequency of nearly 9.78 MHz and
a band width of 1 MHz. The circuitry   (Figure 8) is of
standard design. Mainly weather conditions, ageing of the
active components and environmental vicissitudes, have from
time to time necessiated tuning and tracking of the receiver for
good signal-to-noise ratio and faithful reproduction of the
signal. For signals which are too large or too small the diode
can act nonlinearly and give faulty signal levels. The goodness
of the receiver linearity for the range of signals of our
interest is checked from time to time as follows. The pulse
sequence is programmed to give an echo monitoring the strength
of equilibrium magnetization. This echo amplitude is propor-
tional to the number of resonating spins in the sample. Direct
linear relationship between the signal strength and the number
of spins in the coil which is in turn proportional to $\rho n/M_h$;
where ρ is the liquid sample density, n is the number of
resonating spins per molecule and M_h is the molecular weight
has been found for a variety of samples covering the entire
range of our signal observation   (see **Figure 9**). The
receiver needs good rf-shielding and stout power and signal
connections to avoid any untoward phase detection, noise, *etc.*.

FIGURE 7. PULSE SHAPER

Band width 1MHz, 3db min.
Overall gain 77.5 db, 7500.
Capacitor >1 in pF.
<1 in μF.

Sensitivity for s/n 2:1, 80% modulation, 3 μV.
Max. input signal, 80% modulation, 300 μV.
L, High Q (~80) coil Honeycombwound on ferrite cores.
Recovery time 10 μs.
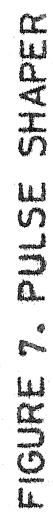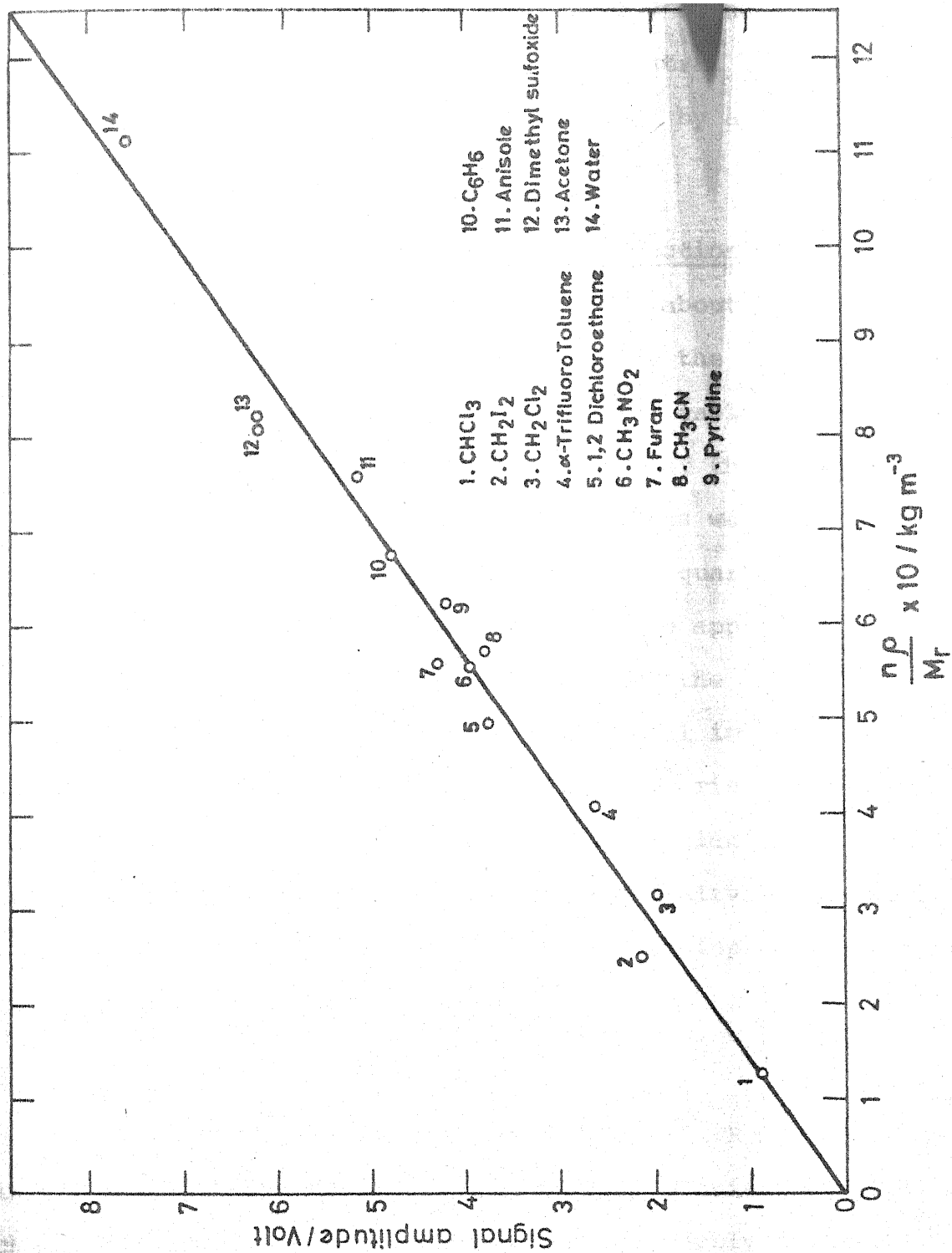
FIGURE 8. RECEIVER

FIGURE 9. RECEIVER LINEARITY CHECK. SIGNAL AMPLITUDE Vs. SPIN DENSITY PLOT.

2.5   Tank Coil

The tank coil consists of closely wound ten turns of SWG 18 copper wire. Positioned in the central region of the magnet, it is fixed to the thermostat lead by about 0.2 m of the same copper wire.

2.6   Transmitter-Tank Coil-Receiver Connection

A coaxial cable length (RG 59/U) about 2.2 m long spans the distance from the transmitter to the tank coil-head BNC T-connector. Another piece of similar cable about 1.0 m long joins the receiver to the other side of the tank coil-head of the BNC T-connector. These cable lengths were chosen by a cut-and-try-method as the use of the exact quarter wave lines (~7.5 m) has proved to be ideal rather than appropriate in real life. The copper wire length between the tank coil and the cryostat lid connector and the non-ideal impedances of the transmitter output and receiver input give rise to a quite complicated theoretical impedance matching problem. In view of this, with an aim to get maximum rf power delivery to the sample and maximum signal delivery to the receiver input the cut-and-try-method has been most practical.

2.7   Magnet

A 12" diameter Varian magnet Model VFR 2703 was used in the present work. Apart from the field variation due to changes in the mean level of the electric supply voltage

(depending on other loads on the electric supply line) and erratic fluctuations, the cooling of the magnet coils has been problematic when the water supply line pressure got low. The Hall probe sensing and regulating the magnetic field has a long cable to the magnet power supply. This long cable if not firmly connected can give field fluctuations due to the contact potential change at the connector head.

2.8 Field Gradient

A steady field gradient at the central region of the magnet is provided by a two coil system, with the coils placed close to the pole faces and having the common axis colinear with the magnet axis (Figure 10). Care must be taken that the sense of current in the coils gives rise to similar poles facing each other. Each of the pair of the coils consists of 50 turns of SWG 20 enamel coated copper wire wound on perspex formers ~7.0 cm in diameter separated from each other by 5.5 cm. A single 1.5 V dry cell is a good power source. A current of 50 mA gives rise to a field gradient of $2.67mT\ m^{-1}$. The change of magnetic field over the sample tube radius 5mm is ~$13\mu T$ which is much smaller than the rf-field amplitude H_1~$600\mu T$ thus satisfying the condition for good gradient field (Woessner (1960)).

2.9 Thermostat

The thermostat is a two-walled Dewar flask. The lid bears the BNC T-connector for the signal line with connections reaching from the tank coil at the bottom. The heater
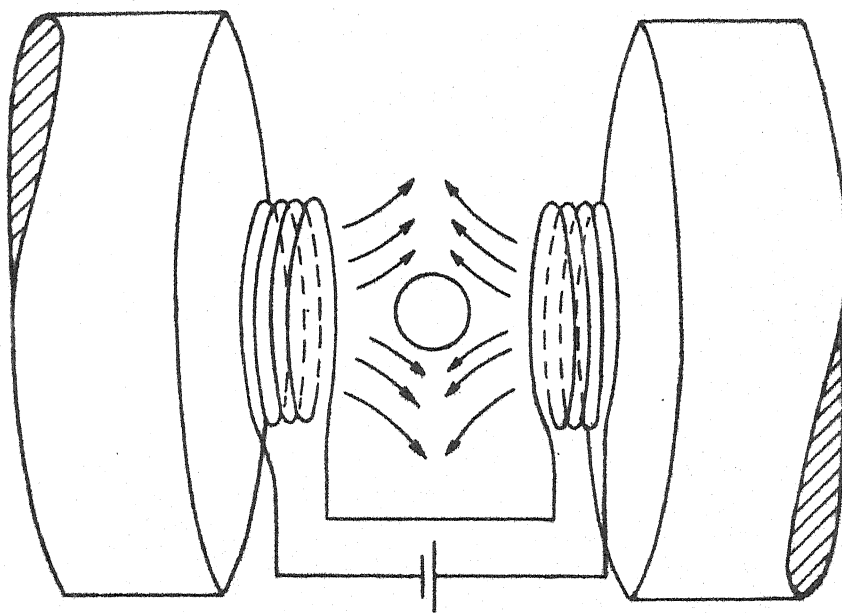
FIGURE 10. FIELD GRADIENT ARRANGEMENT

arrangement inside the thermostat for the sample heating is made up of nonmagnetic high resistance Eureka wires. Two identical heaters in series flank the sample tube symmetrically. Each of the heaters consists of two layers of the heater wire of equal number of turns. The sense of winding of one layer is opposite to that of the other so that the net magnetic field produced by each heater system is zero. Nonvanishing fields will greatly disturb the reckonable gradient field imposed for the self-diffusion coefficient measurement. The heater leads are taken out through the thermostat lid. A copper-constantan thermocouple is taken through the thermostat lid for the junction to sit on the sample and monitor the sample temperature. Good temperature stabilization of the sample is achieved within fortyfive minutes of maintaining a constant dc. The temperature gradient along the sample inside the thermostat sometimes gives violent convection currents in the liquid which is detrimental to the measurement. Such occurrences are scrupulously avoided by maintaining a constant temperature along the sample by means of proper thermal contacts. Onset of convection gives a lower D. (See Carr et al (1954), Kosfeld (1968).

2.10 Sample Preparation

Good grade reagents (mostly of spectroscopic grade) obtained from commercial sources are doubly distilled to start with in order to get rid of dissolved and suspended impurities. Further processing is done in borosilicate glass sample tubes

which can withstand the internal vapour pressure at high temperature (~60atm at the highest temperatures ~200 ^{0}C) (see Figure 11). Above the bulb L containing the liquid there is sufficient free space (FS) to maintain liquid-vapour co-existence at the experimental temperatures. The free space volume (FS) at room temperature is so chosen that the sample volume at critical temperature fills the entire tube volume V (L + FS). The ratio of the sample liquid volume V (L) to the entire sample tube volume V (L + FS) equals the ratio of critical density of the sample to the density at room temperature. There is a small well near the bottom of the tube into which is inserted the thermocouple junction for temperature reading. The distilled sample charged to the required level of the sample tube is frozen and the tube attached to the vacuum line capable of achieving a pressure of nearly 10^{-3} Torr. The gas above the frozen liquid is evacuated. After a while the sample tube is isolated and the frozen liquid allowed to thaw. Because of the low pressure in the region FS dissolved gases in the liquid boil out. Subsequent re-freezing of the liquid in region L and evacuation removes these boiled out gases. Five or six such freeze-pump-thaw cycles proved adequate to divest the sample of any sizeable, highly disturbing paramagnetic oxygen gas impurity, after which the tube is sealed at S_1. Then the highly reactive barium getter G is fired to capture all the residual released gases. Finally the sample tube is sealed at S_2 and separated. The pressure at the top of the frozen sample is now better than 10^{-3}Torr.

To Vaccum line

S_1

S_2

G

FS

L
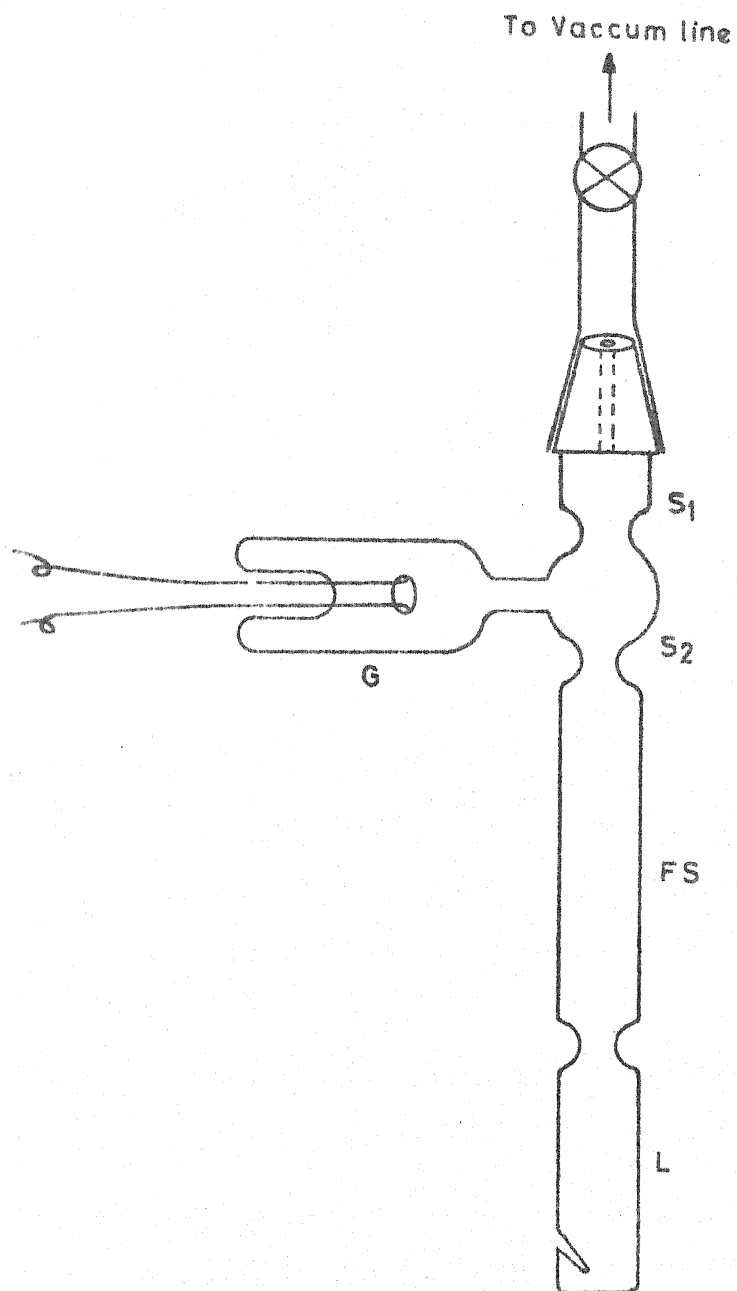
FIGURE 11 - SAMPLE TUBE

2.11   Spectrometer Tuning

The magnet and the electronic system gets stabilized in half an hours time.   Before observing the nmr signal the spectrometer is tuned as follows.   The transmitter output level is set at about ~300V rf.   The receiver band width and centre frequency are also checked by using a cw rf generator.   This makes the transmitter-receiver system ready for the actual signal.

With the connections for signal flow made as shown in Figure 2 a vial of glycerine or tap water doped with a speck of a paramagnetic salt is placed inside the sample coil with the entire coil volume filled.   A single pulse, a microsecond or two wide, is fed to the pass gate, repeating at an interval of one second.   The magnetic field is now slowly increased with an eye on the oscilloscope screen.   With the approach of the resonance frequency beat patterns appear on the screen. Exactly at resonance the beat frequency is zero with a long tail and hence the resonance is very easily discernible.   The width of the pulse is now increased to a value which gives maximum tail height of the free induction decay.   This would correspond to a 90^0 pulse.   Several alternate pulse width and field settings are necessary to be at resonance and to get an exact 90^0 pulse.   Next the 90^0 pulse is removed from the pass gate and the pulse channel which will give a 180^0 pulse is coupled in.   The 180^0 pulse setting is made with the

visual monitor such that the tail height for a 180^0 pulse
is zero. The receiver, going dead for a while after the
large rf pulse, is unable to see the signal during the dead
time. Hence it becomes difficult to monitor the exact tail
height, and the 180^0 pulse setting is slightly arbitrary.
However, the settings of the 90^0 and 180^0 pulses which are
slightly off do not create any perceptible problem in subse-
quent measurements described below.

2.12   Signal Display and Measurement

Echoes are convenient to display and measure, and
are free of receiver dead time. They are therefore better
suited than free induction decays. The echo is stored on
a Tektronix Model 549 storage oscilloscope screen. The
height of the echo from the average base line is measured by
a divider and scale. In the two-pulse 90^0-t-180^0 setting,
if the interval t is short enough to give any reckonable
relaxation, the echo height is a monitor of the equilibrium
magnetization and is proportional to the number of resonating
spins.

2.13 T_1 Measurement

A 90^0-t-90^0-τ-180^0 pulse sequence where $\tau \ll T_1$ and t
can be programmed is used to give an echo at a time τ after
the last 180^0 pulse. The advantages of an echo measurement
are cited in the previous section. If the resonating nuclei

are symmetrically placed in the molecule they are expected
to have a single relaxation time given by the formula

$$S_z(t) = S(0)(1-e^{-t/T_1}),$$

where $S(0)$ and $S_z(t)$ are the voltage amplitudes of the echo
corresponding to the equilibrium magnetization and the growth
of the longitudinal magnetization at time t respectively.
The method of monitoring the equilibrium magnetization is
described earlier. $S_z(t)$ was measured for at least eight
settings of t. $S(0)$ is measured intermittently. Between
successive measurements of $S_z(t)$ a sufficient time ($\sim 5T_1$)
is allowed so that the spins relax back to their equilibrium
value. A plot of $\log \{S(0)/[S(0) - S_z]\}$ versus t gives a
straight line of slope $(\log e)/T_1$. The accuracy of the
relaxation times thus determined is found to be within 5%.

2.14 D Measurement

A steady field gradient of known value is essential
here whereas the sole purpose of a gradient field in T_1
measurement was for forming manageable echoes. In a two-
pulse 90^0-t-180^0 sequence the echo signal amplitude is
related to the equilibrium value through the relation

$$S_z(t) = S(0) \exp(-\gamma^2 G^2 t^3/12D - t/T_2),$$

where G is the field gradient and others have their usual
meanings. The gradient chosen must be such as to give a

more rapidly varying term than the second term but not so large as to forbid sufficient t range observations. A current of 50 mA through the gradient coils giving rise to a field gradient of magnitude 2.67 mT m^{-1} has been found to be suitable as well as convenient. In view of such a choice of the gradient the foregoing equation may be written as

$$S_z(t) = S(0) \exp(-\gamma^2 G^2 t^3 / 12D).$$

Hence a plot of log $(S(0)/S_z)$ versus t^3 should give a straight line of slope $\gamma^2 G^2 / 12D$ which will yield D if G is known. Mathematical formulae have been in vogue to estimate G. They are derivations for idealized cases bearing little resemblance to real life situations. On the other hand, the procedure used here is to take D of several test samples as stated below (§2.15) and to calculate G from the slope of the log $(S(0)/S_z)$ versus t^3 straight line and the known value of D. The G thus found for the gradient current setting of 50 mA is used for calculating the Ds of samples under test from the observed slopes. The accuracy of such D measurement is 5%. The observed slopes of the straight lines log $(S(0)/S_z)$ versus t^3 at the various working temperatures are multiplied by the ratio of test sample D to its log $(S(0)/S_z)$ versus t^3 straight line slope, to give the sample D at that temperature.

2.15 Test Sample Runs

Two test samples, one of water and the other of benzene, are used from time to time to check on the spectrometer functioning and the data credibility. Before and after each experimental sample run the T_1 and D of the test samples at room temperature are measured to ascertain that the spectrometer behaved well during the experimental sample run. Test sample T_1 and D measured in the way cited above (§ 2.13 and 2.14) are given in Figures 12 and 13. The errors in T_1 and D thus measured are about ±5%. Mills (1971, 1973) lists the various D measurements in these test samples. In water, T_1 measured as a function of temperature is available in Simpson and Carr (1958). In benzene, T_1 measured as a function of temperature are available in Green and Powles (1965), and Powles and Figgins (1965).
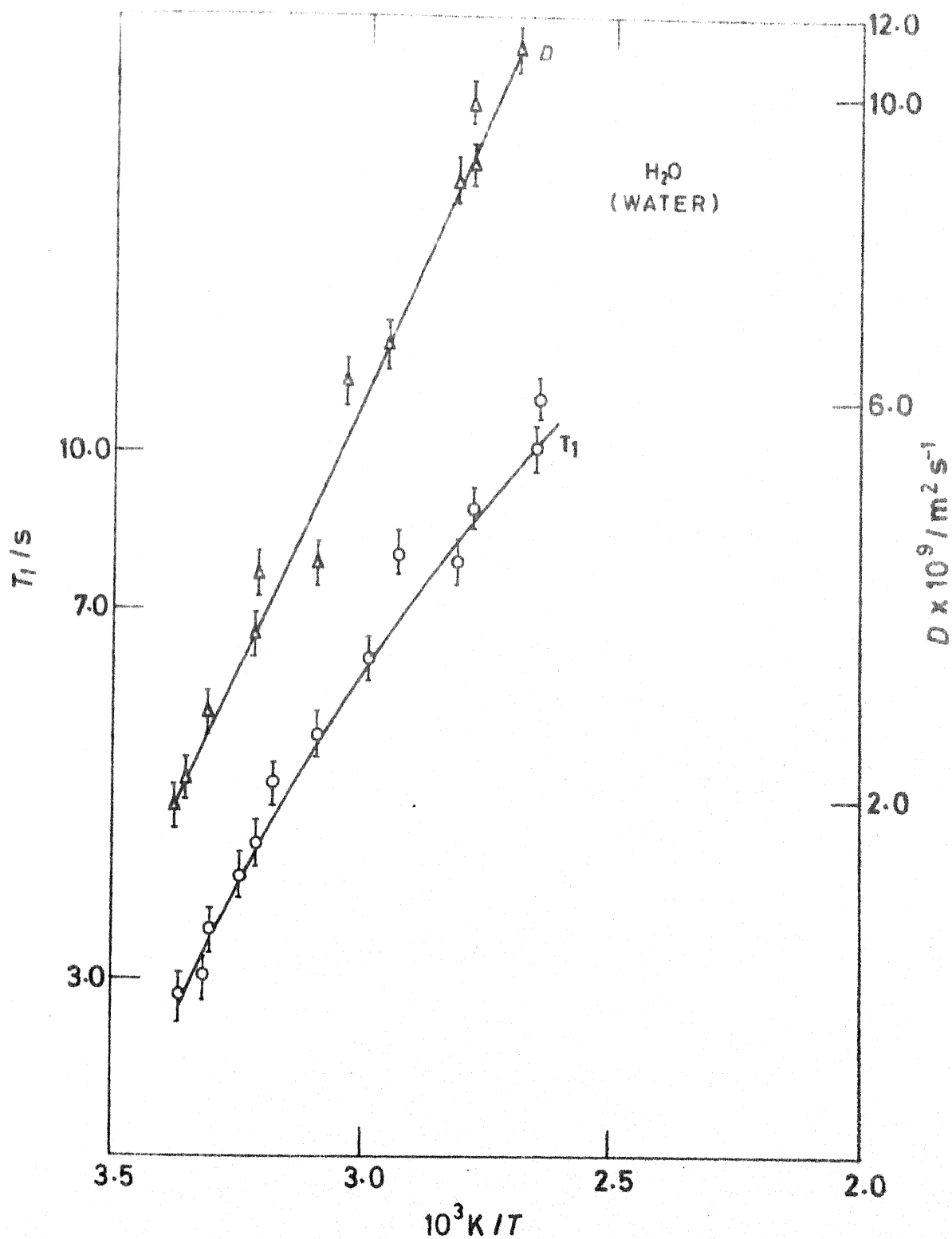
FIGURE 12. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) AND SELF-DIFFUSION COEFFICIENT (D) IN DISTILLED WATER.
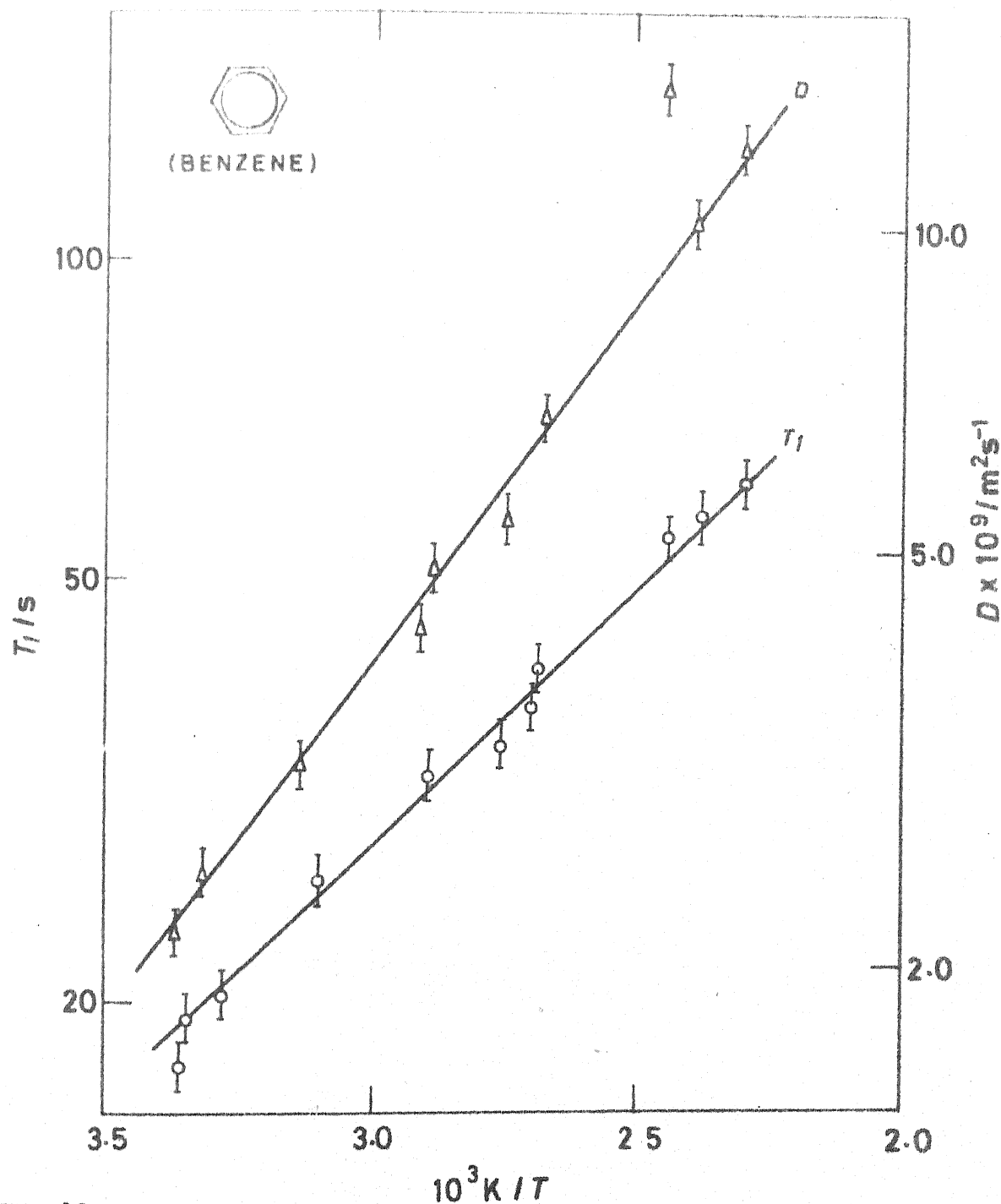
FIGURE 13. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) AND SELF-DIFFUSION COEFFICIENT (D) IN BENZENE.

Coherence is all.

SPIN-ROTATION RELAXATION IN LIQUIDS FOR DYNAMICALLY COHERENT REORIENTATION*

Molecular dynamics, mainly the rotational motion in liquid, is much more intractable than that in gases and solids. In dilute gases the rotational motion is analyzed in analogy with quantum mechanical free rotors. In solids the molecules having been locked to the lattice sites the possible rotational motions are about the well defined molecular axes through well defined angular steps. In liquids the molecular rotational motion can take place about many an axis through unrestricted angular steps where the molecular symmetry axis is itself undergoing orientational changes. To add to the complication, non-spherical molecules too have greater facility for rotating preferentially about the molecular symmetry axis and the rotational anisotropy must be carefully taken into consideration.

As the molecules are energized (say, by increasing the temperature) the orientational changes are much more frequent but the molecule stays in its higher rotational states longer. In other words, the orientational correlation time decreases and the rotational correlation time increases with temperature rise (Gutowsky, Lawrenson and Shimomura (1961). Brown, Gutowsky

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*The work presented in this chapter appears in Chem. Phys. Lett. (1974) <u>27</u> 592.

and Shimomura (1963), Hubbard (1963   Green and Powles (1965)).
The orientational change affects the laboratory frame dipole-
dipole interaction strength through the second order spherical
harmonics $Y_2^m(\theta, \phi)$. Spin-rotation interaction takes place in
the molecular frame, as the molecular rotation involves the
motion of the associated charges and therefore gives rise to a
sizeable magnetic field to couple to the nuclear spin under
observation in the molecule. Since observations are made in
the laboratory frame and the nuclear spins are polarized by
the laboratory magnetic field the molecular rotations must be
transformed to the laboratory frame and in so doing molecular
orientational angles relative to the laboratory frame are
involved. Therefore, the spin-rotation interaction seems to
be both orientation- and rotation-dependent, whereas the intra-
molecular dipole-dipole interaction depends on the orientation
of the dipole-dipole vector in the laboratory frame marked by
the polarizing magnetic field.

At low temperatures and particularly in liquids it is
usually taken for granted that many a molecular collisions go
into randomly changing the molecular orientation through one
radian. Since it has been shown (Huntress (1970), Chandler (1975))
that the collision time approximates the angular momentum
correlation time the present situation is the diffusion case
where $\tau_J \ll \tau_\theta$. In this diffusion limit the fluctuation in
the magnitude of the angular velocity of the molecule has

the predominant contribution to the spin-rotation relaxation rate. As the temperature of the liquid is raised to the neighbourhood of the liquid-vapour critical temperature molecular collisions are less frequent and therefore the persistence of molecular rotation is much longer and in fact $\tau_J \sim \tau_\theta$. But at a temperature much below the critical temperature coherent rotational motions for periods longer than expected are observed (Moniz, Steele and Dixon (1963), Atkins, Loewenstein and Margalit (1969), Miller and Gordon (1970), Kitchlew and Nageswara Rao (1973b), Krishna and Gordon (1974), Mishra and Nageswara Rao (1974)). Such coherent motion will therefore give rise to stronger spin-rotation interaction than that expected in dipolar liquids. It is therefore worthwhile to derive the relation between the spin-rotation relaxation rate and temperature in the case of dynamically coherent motion.

The spin-rotation interaction can be given by a bilinear coupling, $i.e.$ a coupling of the rotational angular momentum of the molecule with the angular momentum of the electrons and then the coupling of the angular momentum of the electrons with the nuclear spins. If $\underset{\sim}{I}$ is the nuclear spin $\underset{\sim}{J}(t)$ the angular momentum whose time-dependence arises due to collisions bringing about changes in it, and C_{ij} are the components of the spin-rotation coupling tensor, the interaction hamiltonian can be given by

$$H' = \underset{\sim}{I} \cdot C \cdot \underset{\sim}{J}, \tag{3.1}$$

in the laboratory frame set up by the polarizing static magnetic field $\underset{\sim}{H}_0$.

In general the coupling tensor is not symmetric and therefore cannot be diagonalized. For the convenience of handling, the coupling tensor C is taken as the sum of a scalar tensor $C^{(0)}$ whose elements are $1/3 \, \mathrm{Tr} \, (C)$, an anti-symmetric tensor of rank one: $C^{(1)}$, whose elements are $C_{ij}^{(1)} = 1/2 \, (C_{ij} - C_{ji})$ and a symmetric tensor of rank two: $C^{(2)}$, whose elements are $C_{ij}^{(2)} = 1/2 \, \{C_{ij} + C_{ji} - 2/3 \, \mathrm{Tr} \, (C)\}$ where C_{ij} is the $(ij)^{\mathrm{th}}$ element of C. Using the index $\ell \, (= 0, 1, 2)$ one can write

$$H' = \sum_{\ell} \underset{\sim}{I} \cdot C^{(\ell)} \cdot \underset{\sim}{J} (t), \tag{3.2}$$

in the molecular frame. In general each component of the hamiltonian in the laboratory frame is given by

$$H'_\ell = \sum_{q=-\ell}^{\ell} (-1)^q \, F_\ell^q (t) \, A_\ell^{-q}, \tag{3.3}$$

where $F^{-q} (t)$ is the time-dependent lattice operator responsible to bring about relaxation of the spin system and A^{-q} are the spin operators. As observations are made in the laboratory frame the foregoing form of the hamiltonian is most suitable in describing the relaxation of the spin system. The rate equation for the spins is given by

$$\frac{d \langle I_z \rangle^I}{dt} = - J(0) \sum_q (-1)^q \, \mathrm{Tr}[A^q, [A^{-q}, I_z]] (\sigma^I - \sigma_0^I), \tag{3.4}$$

where $\langle I_z \rangle^I$ is the expectation value of the spin magnetization

in the field direction, σ_0^I is the equalibrium value of the
density matrix σ^I, (the superscript I denoting the use of the
interaction picture) and $J(0)$ is the usual spectral density
under the extreme narrowing condition, $i.e.$ $\omega\tau\approx 0$, having the form

$$J(0) = J^q (q\omega_0) = \int_0^\infty d\tau <F^*(t) F(t - \tau)>, \qquad (3.5)$$

is independent of both q and ω_0. The important thing to note
here is that under the extreme narrowing condition the integral
of any lattice operator's time correlation function predominant-
ly determines the rate of change of spin magnetization and that
the knowledge of detailed nature of the lattice operator is
not required.

As the molecular frame equation must be changed over to
the laboratory frame in order to put Eq. 3.2 in a form like
Eq. 3.3 the help of Wigner rotation matrices must be taken.
Both I and J are operators of rank one and therefore the
rotation matrices $D^{(1)}$ are of use (Rose (1957)). One then
writes

$$A^q_{\text{molecule-fixed}} = \sum_{q'} D^{(1)}_{q'\,q} (\Omega) A^{q'}_{\text{space-fixed}}, \qquad (3.6)$$

and a similar relation for $F^q(t)$ operators. Inserting
these into Eq. 3.4 one then finally gets

$$-\frac{d}{dt} \langle I_z \rangle = \sum_{\substack{\ell, q, \\ k, m, \\ q', m'}} (-1)^{m+k} C(11\ell, \; m-q \, q \, m)$$

$$C(11\ell, \; m'-q' \, q' \, m') c'^{k} c'^{m'}$$

$$\int_0^\infty d\tau \; \langle J'^{(m-q)}(0) \; \mathcal{D}_{kq}^{(1)*}(0) \; J'^{(-m'+q')}(\tau) \; \mathcal{D}_{k-q'}^{(1)}(\tau) \rangle_{av}$$

$$\mathrm{Tr}\{ [A^{-k}, [A^k, I_z]] (\sigma - \sigma_0) \} , \qquad (3.7)$$

where $C(11\ell, \; m-q \, q \, m)$ etc. are the Clebsch-Gordon coefficients c_ℓ^{m} s are the components of the C_ℓ' tensor in the molecular frame with the rotational angular momentum operator connected to the lattice operator in the molecular frame by

$$F_\ell'^{q} = \sum_{m} (-1)^q C(11\ell, \; m-q \; q \, m) \; c_\ell'^{m} J'^{-m+q}(t). \qquad (3.8)$$

In Eq.3.7 two types of correlation functions are involved. In the first kind the molecular rotation leads to the modulation of the components of C and hence the correlation arising because of C modulation must be noted. In the second kind of the correlation function within the angular brackets of Eq. 3.7 are fairly involved as they simultaneously contain operators pertaining to the angular momentum (i.e. rotational) persistence and the persistence of the orientation of the molecule relative to the laboratory frame. The exact evaluation of this correlation function in the most general case is very involved.

Although the use of $\rho^{(1)}$ matrices comes naturally because of the rank of the operators [I] and [J] involved, transforming to use $\rho^{(2)}$ matrices becomes most useful as $\rho^{(2)}$ happens to be arising most usually in other relaxation mechanisms like the intramolecular dipolar interaction, chemical shift anisotropy, quadrupolar interaction where second rank spherical harmonics come to the fore. The consistent use of $\rho^{(2)}$ for all relaxation mechanisms helps compare the processes from the same platform. This has been successfully achieved by Hubbard (1963). He connects $\rho^{(1)}$ and $\rho^{(2)}$ through the use of j-symbols. Having done so, for a spherical top molecule under the extreme narrowing limit, Hubbard's prescription (Hubbard (1963), Huntress (1968), Marayott, Farrar and Malmberg (1971), McClung (1972)) gives

$$\left(\frac{1}{T_1}\right)_{SR} = \frac{2 I k T}{\hbar^2} \left(C_d^2 \, \tau_{J_1} + 2 C_a^2 \, \tau_{J_2} \right) , \qquad (3.9)$$

where I is the moment of inertia, k is the Boltzmann constant, T is the temperature and C has as axis of symmetry such that

$$C_t = \{ C_\parallel + 2 C_\perp \}/V^{\frac{1}{3}}, \quad C_a = \{ C_\parallel - C_\perp \}/3 ,$$

where $C_\perp, C_\parallel$ are the corresponding perpendicular and parallel components. The use of $\rho^{(2)}$ gives as usual an explicitly angular momentum dependent correlation function related to the angular momentum correlation time

$$\tau_{J_1} = \int_0^\infty \frac{<J(0) \cdot J(t)>}{<J^2(0)>} \, , \qquad (3.10)$$

and a complicated correlation function $<J^{q*}(0) D_{qm}^{(2)*}(\phi,0) J^{q''}(t)$
$D_{q'm'}^{(2)}(\phi',t)>$ like the one in Eq. 3.7 related to a correlation
time τ_{J_2} involving integrals like

$$\int_0^\infty <J^*(0) D_{qm}^{(2)*}(\phi,0) \ J^{\alpha'}(t) \ D_{q'm'}^{(2)}(\phi',t)> dt \ .$$

Like the correlation function in Eq. 3.7 handling the
correlation function in the foregoing equation in the most
general case is equally difficult. Separation of the angular
momentum and orientation dependent parts is only achieved in
extreme limits where such mutual dependence is greatly decoupled.
The solution at such convenient limits is shown in the following.

For such limit consideration, a knowledge of the free
molecular period is of great help. The inertia and thermal
energy of the molecule determine the free period of rotation
given by $\tau_0 = (I/kT)^{1/2}$. Also of use is the correlation time
τ_J , a measure of fluctuation of the magnitude of the angular
velocity $|\omega|$, given by a rotational diffusion equation
$\tau_J = I D_{rot}/kT$. Two other correlation times of importance are
τ_{θ_1} and τ_{θ_2}. Correlation time τ_{θ_1} is the one that arises in
dielectric measurements giving us a measure of the orientational
correlation of the dipolar axis through the integral of the
correlation function of the spherical harmonic Y_1^m. The
correlation time τ_{θ_2} arises in the strength of intramolecular
dipolar interaction, quadrupolar interaction, chemical shift

anisotropy interaction *etc.* in nmr measurements giving us a measure of the orientational correlation of the appropriate vector pertaining to the interaction through the integral of the correlation function of the spherical harmonic Y_2^m .

In the diffusion limit many a molecular collisions are necessary finally to give a random orientational change by one radian. Therefore the collision time which is a measure of τ_J is much shorter than τ_{θ_1} and τ_{θ_2} the orientational correlation times. During τ_J, therefore, the orientation dependent $D^{(2)}(\theta, t)$ does not change appreciably. Two distinct simplifications arise thereof. First, J and $D^{(2)}$ in Eq. 3.11 are decoupled, and second, the constancy over the period leads to unit correlation, *i.e.* $D^{(2)}$s are completely correlated over the interval. Hence the relation in Eq. 3.11 simplifies to that Eq. 3.10 giving $\tau_{J_1} = \tau_{J_2} = \tau_J = I D_{rot}/kT$. Now insertion of the τ_{J_1} and τ_{J_2} values into Eq. 3.9 leads to the relation

$$(1/T_1)_{SR} \propto D_{rot} . \qquad (3.12)$$

It has further been shown (see for example Abragam (1961) p.299) that the diffusion equation leads to

$$\tau_{\theta_1} = 1/2 \ D_{rot} \text{ and } \tau_{\theta_2} = 1/6 \ D_{rot}.$$

As mentioned earlier, since τ_{θ_2} is directly proportional to intramolecular dipolar interaction and hence to the corresponding relaxation rate, one can write for the dipole-dipole

relaxation rate

$$1/T_{1\,d-d} \propto 1/\mathcal{D}_{rot}. \qquad\qquad (3.13)$$

The rotational processes being temperature-activated,
Eqs. 3.12 and 3.13 show opposite temperature-dependence for
the spin-rotation and intramolecular dipolar relaxation rates
in the diffusion limit.

In the inertial limit, which is supposed to be achieved
near the liquid-vapour critical temperature, the rotational
motions are dynamically coherent (Steele (1963), Atkins (1969)), $i.e.$
they occur for times comparable to orientational correlation
time and molecular free rotation time, $i.e.$ $\tau_J \sim \tau_{\theta 1,2} \sim \tau_{\theta}$.
The separation of pure rotation and reorientation parts as in
the diffusion limit is not possible as J and $\mathcal{D}^{(2)}$ have similar
characteristic times and are thought to be very well coupled
mutually. The free rotational motion is described as arising
due to small rotational friction. A collision-governed diffu-
sion equation fails to describe the rotational motion in this
limit. To handle this problem Steele (1963) used a rotational
Langevin equation which is nothing but Newton's second law
with rotational friction effects properly considered. The
diffusion limit definition of $\tau_J = I\mathcal{D}_{rot}/kT$ is discarded in
favour of $\tau_J = I/\xi$, where ξ is the rotational friction
coefficient. Steele shows that in the region $1/3 < \xi/(IkT)^{1/2} < 2$,
$\tau_{\theta\ell}$ approximates very well the integral of the free rotor

correlation functions which are gaussian. These results of
Steele have also been arrived at by Hubbard (1972) independently.
The Gaussian decays of the free rotor correlation function give

$$\tau_{\theta 1} = \pi^{1/2}/2 \ \tau_{\oint} = 1/2 \ (\pi I/kT)^{1/2} \qquad \text{and}$$

$$\tau_{\theta 2} = 1/2 \ (\pi/3)^{1/2} \ \tau_{\oint} = 1/2 \ \pi I/3kT)^{1/2}, \qquad (3.14)$$

i.e. $\tau_{\theta 1}, \ \tau_{\theta 2} < \tau_{\oint}$. Further the limit $\xi/(IkT)^{1/2} < 1$ implies
$\tau_{\oint}/\tau_J < 1$ giving finally the relation $\tau_{\theta 1}, \ \tau_{\theta 2} < \tau_{\oint} < \tau_J$.
$\tau_{\theta 1}, \ \tau_{\theta 2}$ being now the smallest of all the correlation times,
i.e. the orientational changes being quicker than the rotational
changes, the orientational dependence (i.e. the nature of $\tau_{\theta 1}$,
$\tau_{\theta 2}$) predominantly governs τ_{J_1} and τ_{J_2}. We have, therefore,
from Eq. 3.14 and as both $\tau_{\theta 1}$ and $\tau_{\theta 2}$ vary as $T^{-1/2}$, τ_{J_1} and
τ_{J_2} must both vary as $T^{-1/2}$. In Eq. 3.9 the spin-rotation
relaxation rate is seen to be proportional to $\tau_J T$. Hence
using the foregoing temperature-dependence of τ_J the spin-
rotation relaxation rate in the inertial limit will vary as
$T^{1/2}$. The intramolecular dipolar relaxation being proportional
to $\tau_{\theta 2}$ will vary as $T^{-1/2}$ (vide Eq. 3.14) in the inertial
limit. In many dipolar liquids where both spin-rotation and
intramolecular dipolar interactions are active relaxation
mechanisms the slow increase of spin-rotation relaxation
rate with temperature (as $T^{-1/2}$) must give an essentially
constant total dipolar relaxation rate over a large temperature
range. The experimental observation of such a broad maximum

in total intramolecular relaxation rate would then hint
at the presence of dynamically coherent reorientational
motion.

Beyond the inertial limit one gets to the dilute gas
region where the rotational coherence time is much longer
than the free rotational time. As stated earlier this
helps (Bloom, Bridges and Hardy (1971)) in considering
the molecular system as a collection of quantum mechanical
free rotors and in finding that τ_{J_1} and τ_{θ_2} are linearly
related. The present observation that τ_{J_1} and τ_{J_2} are
proportional to τ_{θ_1} and τ_{θ_2} in the inertial limit is in
the same ball park as the observations of Bloom, Bridges
and Hardy (1971) and our results seem to be qualitatively
correct (vide Chapters 4 and 5). The limited importance
of such qualitative agreement must be borne in mind as
the present discussion is based on the classical model
of reorientation of the spherical rotors whereas the
consideration of Bloom et al pertains to the quantum
mechanical model of the free rotors. Other corroborating
evidence to the τ_{J_1} , τ_{θ_2} inverse relationship in the
Debye limit and direct relation in the inertial limit comes
from McClung (1969, 1972).

Thou shalt not methylate thy spirit.

CHAPTER 4

STUDIES IN SOME METHYL GROUP CONTAINING MOLECULAR LIQUIDS

Investigations into the molecular motion in a group
of compounds; methyl iodide (CH_3I), acetonitrile (CH_3CN),
nitromethane (CH_3NO_2), acetone (CH_3COCH_3) and dimethyl sulfoxide
(CH_3SOCH_3) are reported in this chapter. Of these, methyl
iodide and acetonitrile are symmetric top molecules. The
barriers to the methyl group rotation in others are as follows:
CH_3NO_2 6.03 cal/mole and CH_3COCH_3 0.778 kcal/mole (Wolrab
(1967)); CH_3SOCH_3 2.2 kcal/mole (Lyerla and Levy (1974)). The
working temperature range (300K to 450K) corresponds to a
thermal energy range of nearly 0.6 to 1.0 kcal/mole as a result
of which in all except the dimethyl sulfoxide the internal
motion will be sufficiently activated. These molecules are
fairly light ones with small moments of inertia, small root
mean square angular momentum and are therefore possible
candidates for a good deal of free rotation and consequent
spin-rotation interaction (Herzberg (1950), Rugheimer and
Hubbard (1963), Hackleman and Hubbard (1963)). Although none
of these molecules are light enough to satisfy $\sqrt{<J^2>}$ less than or
equal to 5 (the condition for inertial motion), the possibility
of fast motion about the methyl group symmetry axis makes the
rotational coherence a possible governing factor for the

relaxation. The moments of inertia (I_A, I_B, I_C) about the principal molecular axes are as follows:

Compound	$I_A \times 10^{47}$ $kg^{-1}m^{-2}$	$I_B \times 10^{47}$ $kg^{-1}m^{-2}$	$I_C \times 10^{47}$ $kg^{-1}m^{-2}$	Source of data
CH_3I	5.5	5.5	111.9	Lyerla *et al* (1971)
CH_3CN	5.5	5.5	91.1	Lyerla *et al* (1971)
CH_3NO_2	62.9	79.6	142.8	Cox and Waring (1972)
CH_3COCH_3	49.8	59.4	103.0	Koga *et al* (1973)
CH_3SOCH_3	119.0	119.3	121.5	Feder *et al* (1969)

At the out set remarkable asymmetry in the moments of inertia of CH_3I and CH_3CN are prominent from the preceding table and hence some large rotational asymmetry in molecular motion is envisaged. Also expected is the large preponderant intramolecular relaxation over the intermolecular relaxation. Zens and Ellis (1975) establish an empirical relation between the spin-rotation relaxation rate and the internal rotation barriers. The molecules of present interest are expected to give sizeable spin-rotation interaction contribution.

Apart from the general interest in investigating into the translational, reorientational and rotational motions, the added complication due to the superposition of the internal rotation on the overall molecular rotation is noticed.

The T_1 and D measured over suitable temperature ranges for the present series of compounds are shown in Figures 14 to 21. Some of the general observations regarding molecular dynamics which can be made from the look of these curves are as follows. The slow decrease of T_1 with temperature rise in CH_3I and CH_3CN (Figures 14 and 15), suggests surrounding independent free motion and the presence of large spin rotation interaction. The relaxation time of nitromethane increases very slowly with temperature (Fig. 16) and inertial motions are envisaged. The T_1 variation with temperature in acetone (Fig. 18) is moderate and is in keeping with the asymmetric molecular shape with consequent collision limited temperature sensitive process. The bold T_1 variation with temperature in dimethyl sulfoxide (Fig. 20) could be an outcome of a collision limited process. Self-diffusion coefficients in all these compounds seemingly obey the Arrhenius relation

$$D = D(0) \exp(-E/RT) , \qquad (4.1)$$

where $D(0)$ is a constant, and E is the activation energy over their respective temperature ranges of study. The limited temperature range of observation and the errors in D measurement makes it particularly hazardous to vouch for the $D(0)$ and E parameters. Nevertheless, as some authors quote the self-diffusion activation energies for some of the presently discussed compounds, the calculated activation energies from our data are presented in Table 4.1 for the purpose of comparison.

FIGURE 14. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) AND SELF-DIFFUSION COEFFICIENT (D) IN METHYL IODIDE.
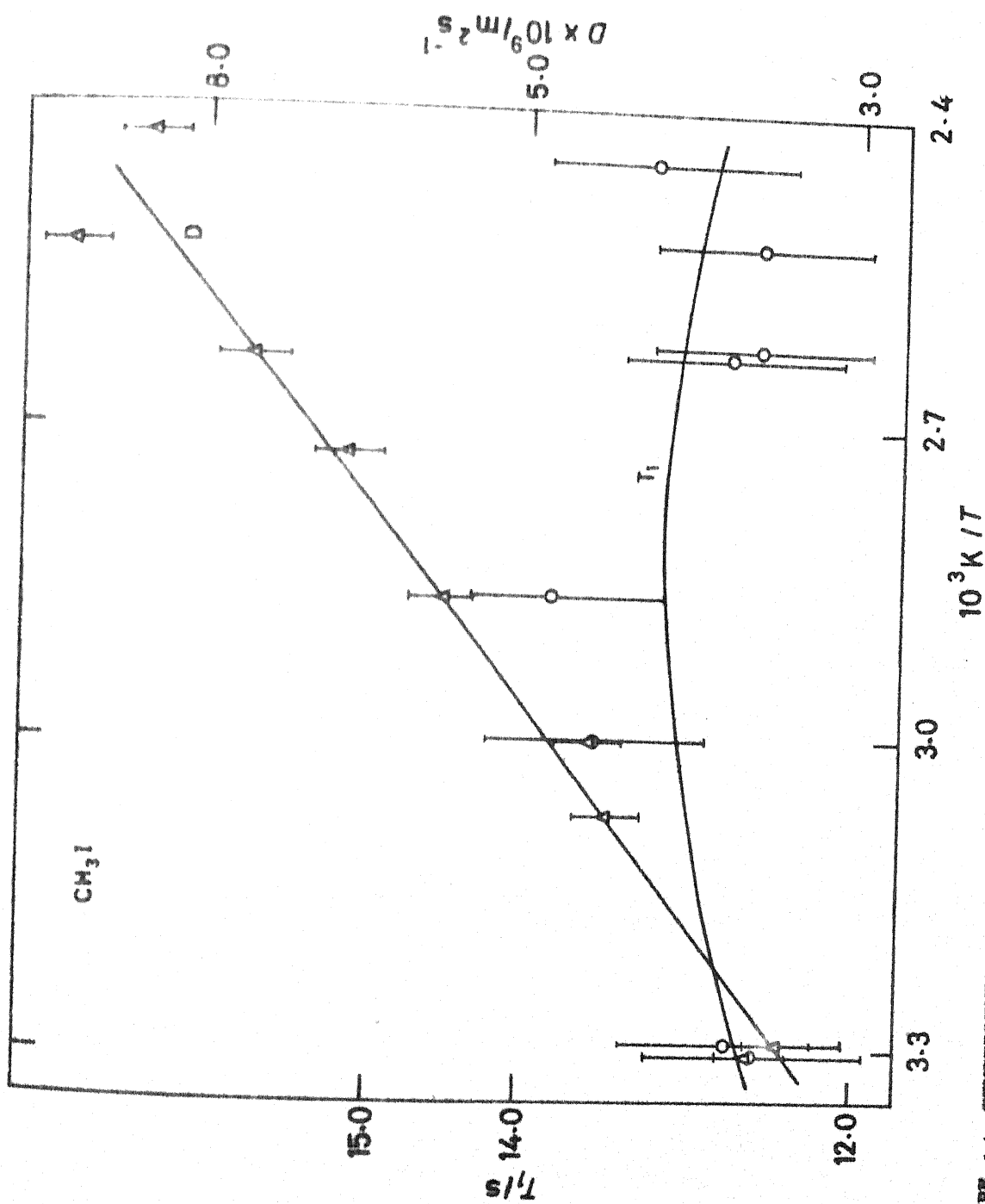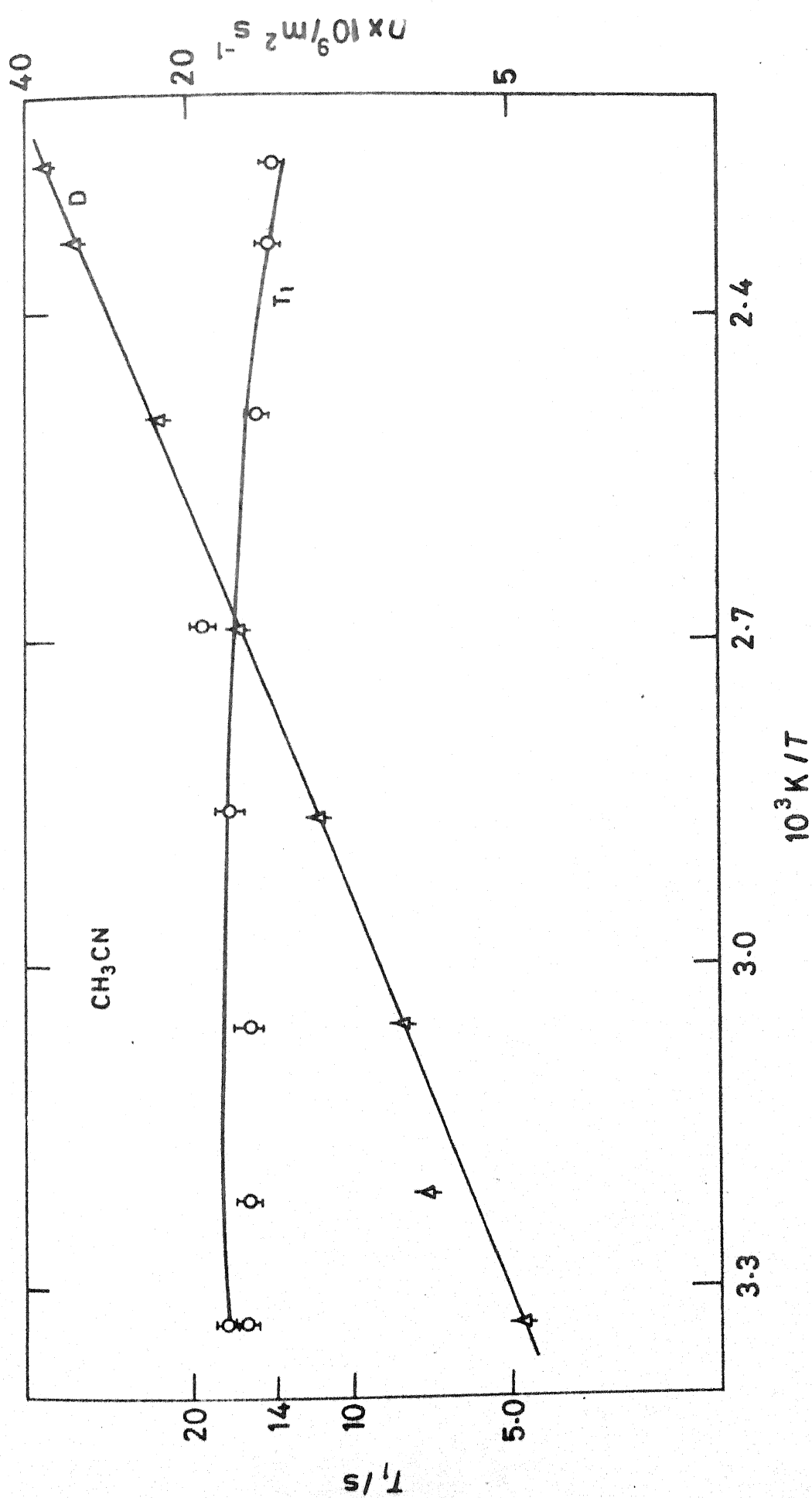
FIGURE 15. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) AND SELF-DIFFUSION COEFFICIENT (D) IN ACETONITRILE.
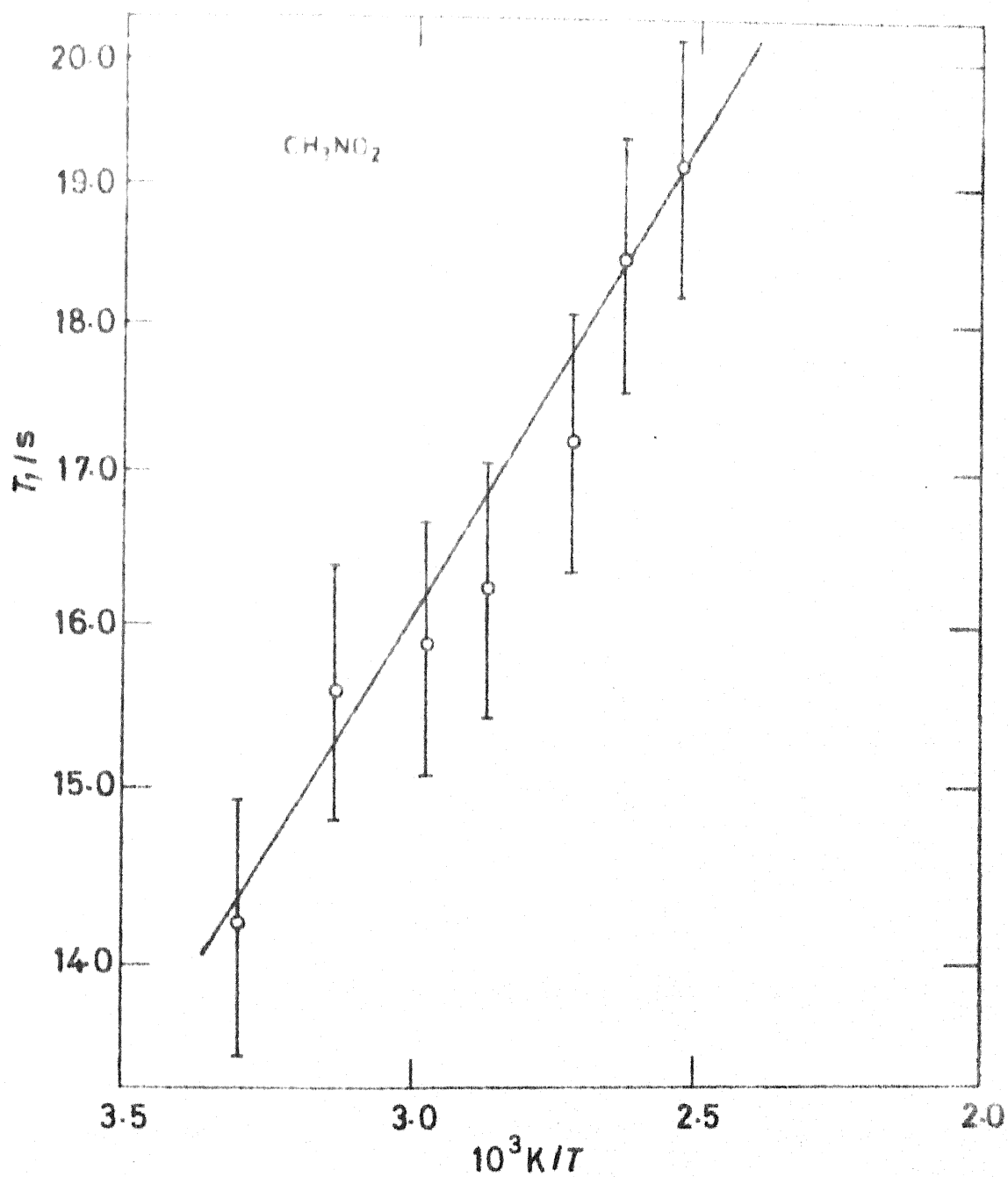
FIGURE 16. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) IN NITROMETHANE.
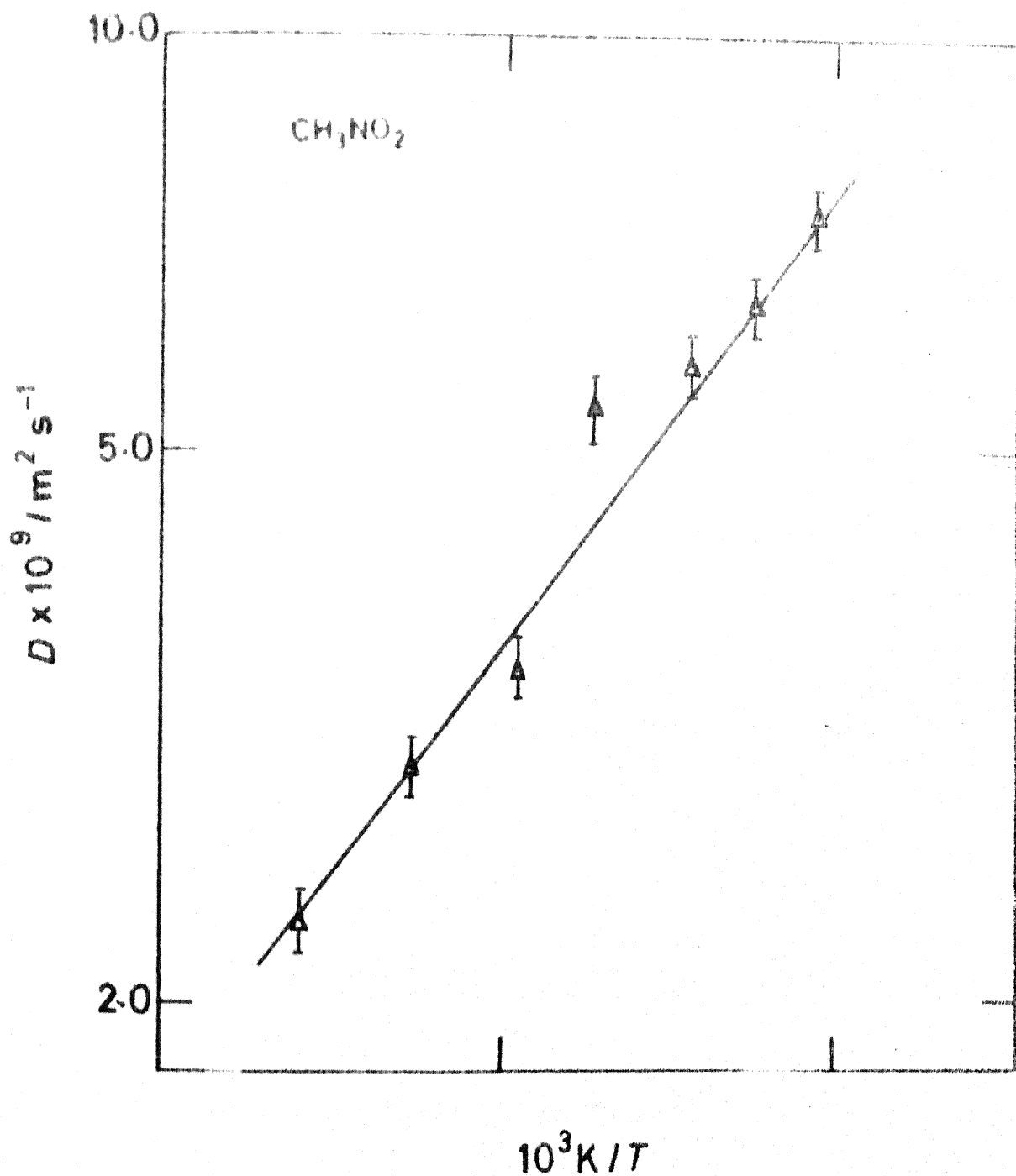
FIGURE 17. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN NITROMETHANE.
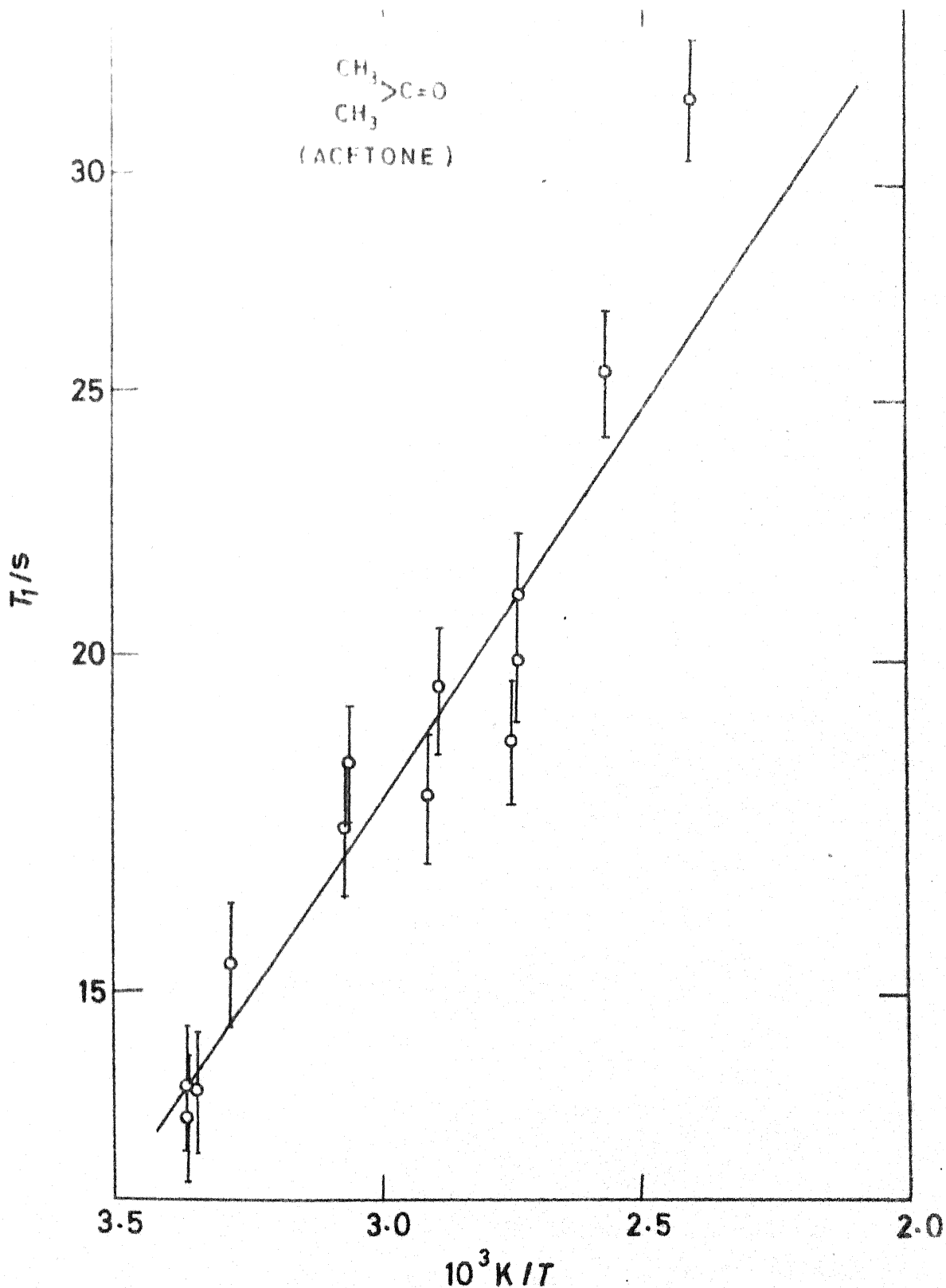
FIGURE 18. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) IN ACETONE.
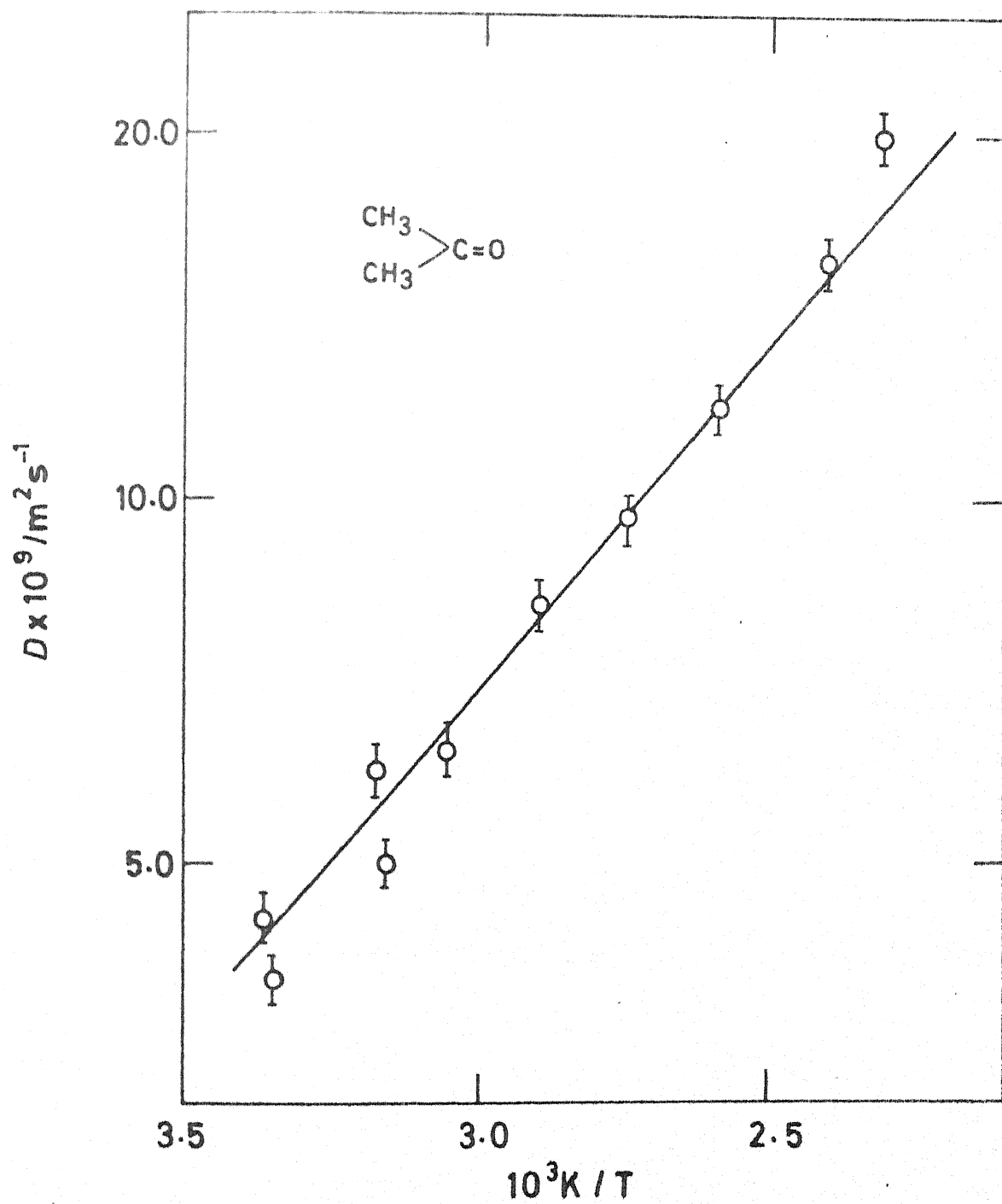
FIGURE 19. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN ACETONE.
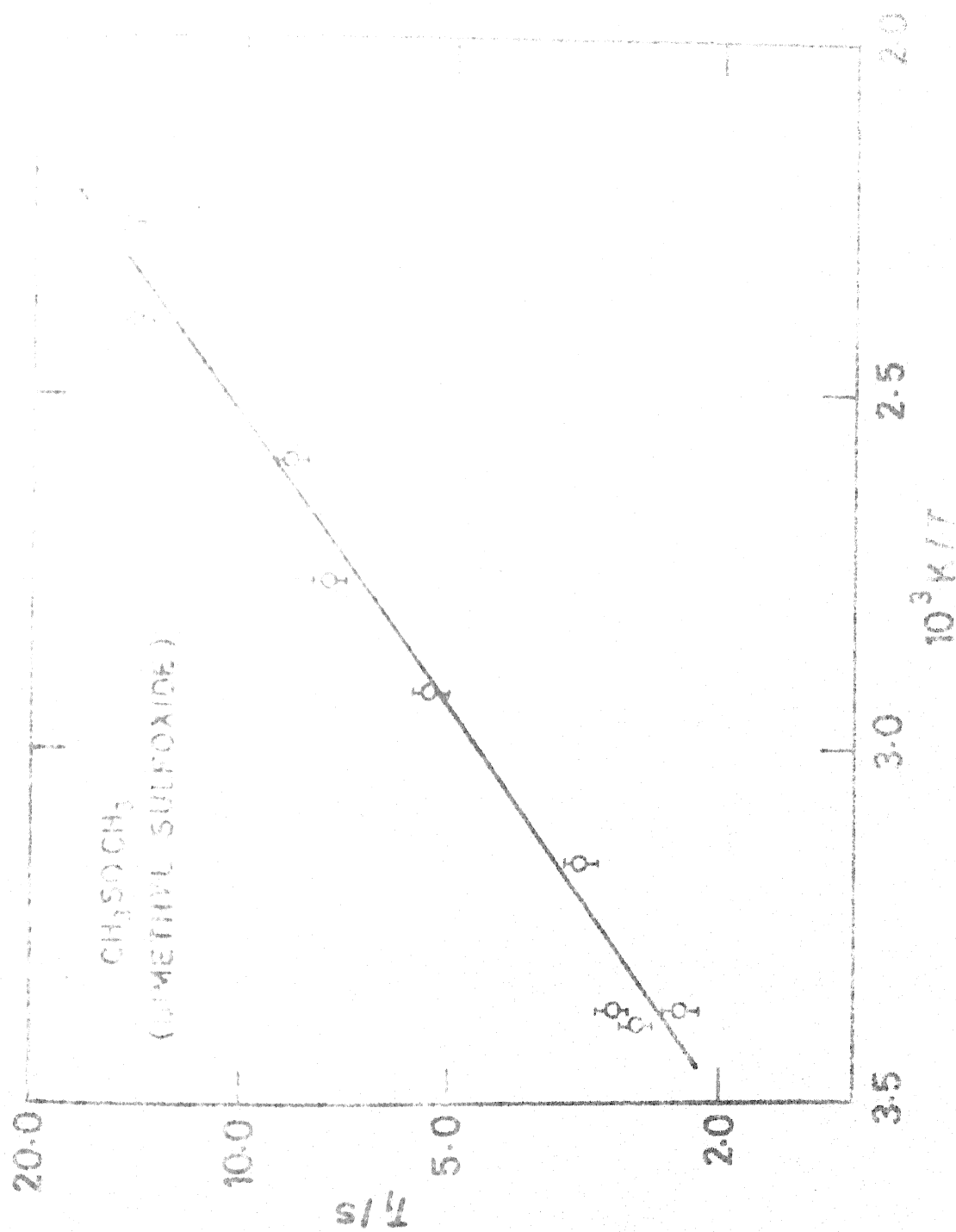
FIGURE 20 - TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) IN DIMETHYL SULPHOXIDE.
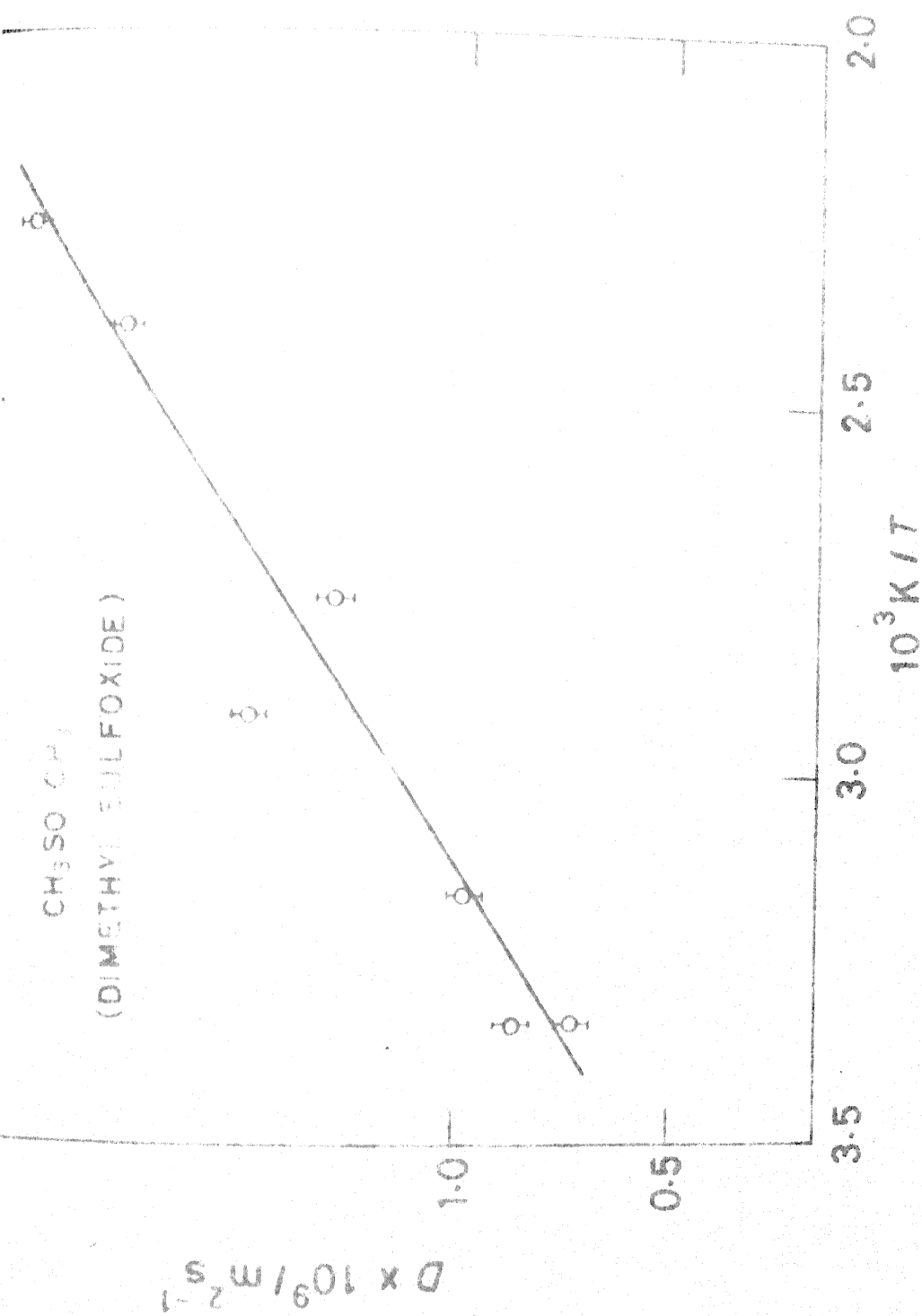
FIGURE 21. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN DIMETHYL SULPHOXIDE.

TABLE 4.1

THE ACTIVATION ENERGIES OF THE VARIOUS PARAMETERS IN THE METHYL GROUP CONTAINING COMPOUNDS

Compound	$E(D)$ $(kcal)^{-1}$. mole	$E(\eta)$ $(kcal)^{-1}$. mole	$E(\rho/D)$ $(kcal)^{-1}$. mole	$E(\eta\rho/T)$ $(kcal)^{-1}$. mole	$E(T/\eta)$ $(kcal)^{-1}$. mole	$E(\eta/T\rho)$ $(kcal)^{-1}$. mole	$E(R_{1intra})$ $(kcal)^{-1}$. mole	$E(R_{1tot})$ $(kcal)$ mole
CH₃I	2.42	1.51	2.75	2.62	2.28	2.05	-	-
CH₃CN	3.65	1.83	4.26	3.10	2.28	2.19	-	-
CH₃NO₂	3.02	2.12	3.34	3.26	2.83	2.48	-	0.85
CH₃COCH₃	2.58	1.82	3.03	3.08	2.61	2.18	0.80	1.35
CH₃SOCH₃	2.86	3.18	2.56	-	-	-	3.70	3.37

$E(D)$ and $E(T/\eta)$ are obtained from the corresponding linear plots obeying $E(X) = -R\frac{\partial \ln X}{\partial 1/T}$,

where X stands for D and T/η, and $E(\eta)$, $E(\rho/D)$, $E(\eta\rho/T)$, $E(\eta/T\rho)$, $E(R_{1intra})$, and $E(R_{1total})$ are

obtained from the corresponding linear plots obeying $E(Y) = -R\frac{\partial \ln Y}{\partial 1/T}$, where Y stands for η, ρ/D

$\eta\rho/T$, $\eta/T\rho$, R_{1intra} abd R_{1total}.

The error in the activation energy calculation is about 5%.

As the various relaxation rates, comprising the total observed relaxation rate, are harbingers of different correlation times and motional processes it is imperative that they are first separated. As argued in Chapter 1 (p.31), Torrey's relation (Eq.1.10) gives good estimate of the intermolecular dipolar interaction contribution to the relaxation. With the help of D observed *in situ* the molecular radius is first estimated using the Stokes-Einstein relation (see the Appendix) and then used in $(1/T_1)_{inter}$ estimation. The density and viscosity data necessary for such calculations are culled out from the following sources:

Compound	Density data available in the temperature range	Source of the data
CH_3I	0 °C to 40 °C	*Int. Crit. Tables* (1928a)
CH_3CN	-45 °C to 60 °C	*ibid.* (1928b)
CH_3NO_2	0 °C to 100 °C	*ibid.* (1928b)
CH_3COCH_3	0 °C to 50 °C	*ibid.* (1928b)
CH_3SOCH_3	20 °C to 80 °C	Schläfer *et al* (1960)
	Viscosity data available in the temperature range	
CH_3I	0 °C to 40 °C	*Int. Crit. Tables* (1930a)
CH_3CN	16.6 °C to 81.5 °C	*Landolt-Börnstein* (1969a)
CH_3NO_2	0 °C to 85 °C	*Int. Crit. Tables* (1930a)
CH_3COCH_3	0 °C to 54 °C	*ibid.* (1930b)
CH_3SOCH_3	20 °C to 80 °C	Schläfer *et al* (1960)

Since η and ρ are not available over the entire working temperature range, they are suitably extrapolated to be of use in the calculation.

The intermolecular relaxation rates of all these compounds thus calculated seemingly obey an Arrhenius relation (see Figs. 22 to 26). The activation energies for the intermolecular relaxation rates are given in Table 4.1. The difference between the total and intermolecular rates give the total intramolecular relaxation rate (plots in Figs. 22 to 26). It is seen that the intramolecular relaxation rates of CH_3I, CH_3CN and CH_3NO_2 increase with temperature as would be expected in the event of dominant spin-rotation interaction. It is rather unfortunate that even though intramolecular dipolar and spin-rotation interactions are the contributing factors to the total intramolecular relaxation rate, the experiment does not show the distinct trough in the relaxation rate *versus* temperature plot which would facilitate the separation of the two constituent relaxation rates as they would be equal at the trough of the plot. Even in the absence of such a situation the trend of variation of the various parameters as described below also hint at the molecular dynamics.

As the rotational and reorientational parts of the total intramolecular relaxation could not be separated, an effective reorientational correlation time is defined to give a handle on the general rotational situation. The intramolecular dipolar
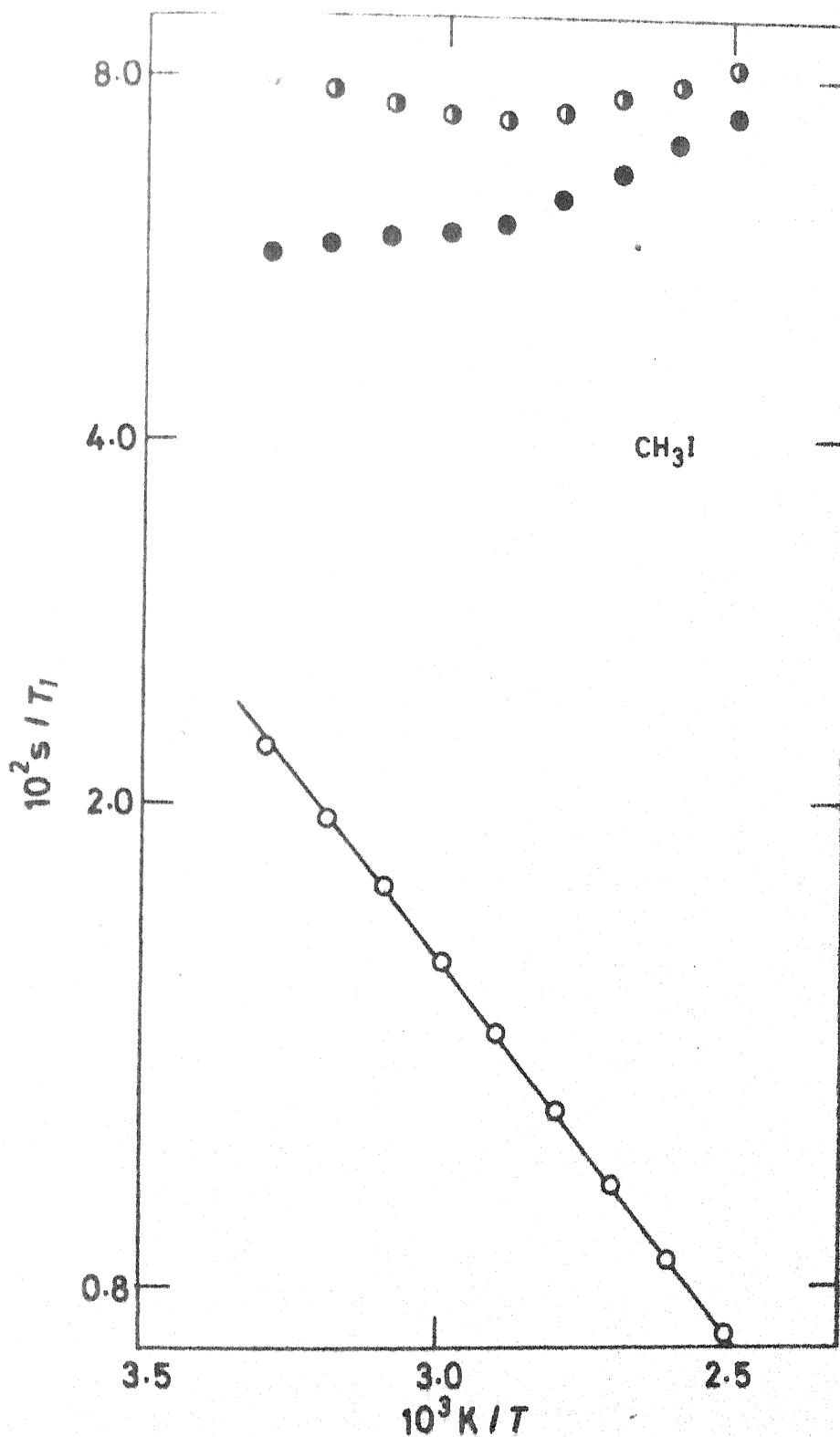
FIGURE 22. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN METHYL IODIDE. ◐ , TOTAL RELAXATION RATE (OBSERVED). ○ , INTERMOLECULAR RELAXATION RATE (CALCULATED). ● , INTRAMOLECULAR RELAXATION RATE.
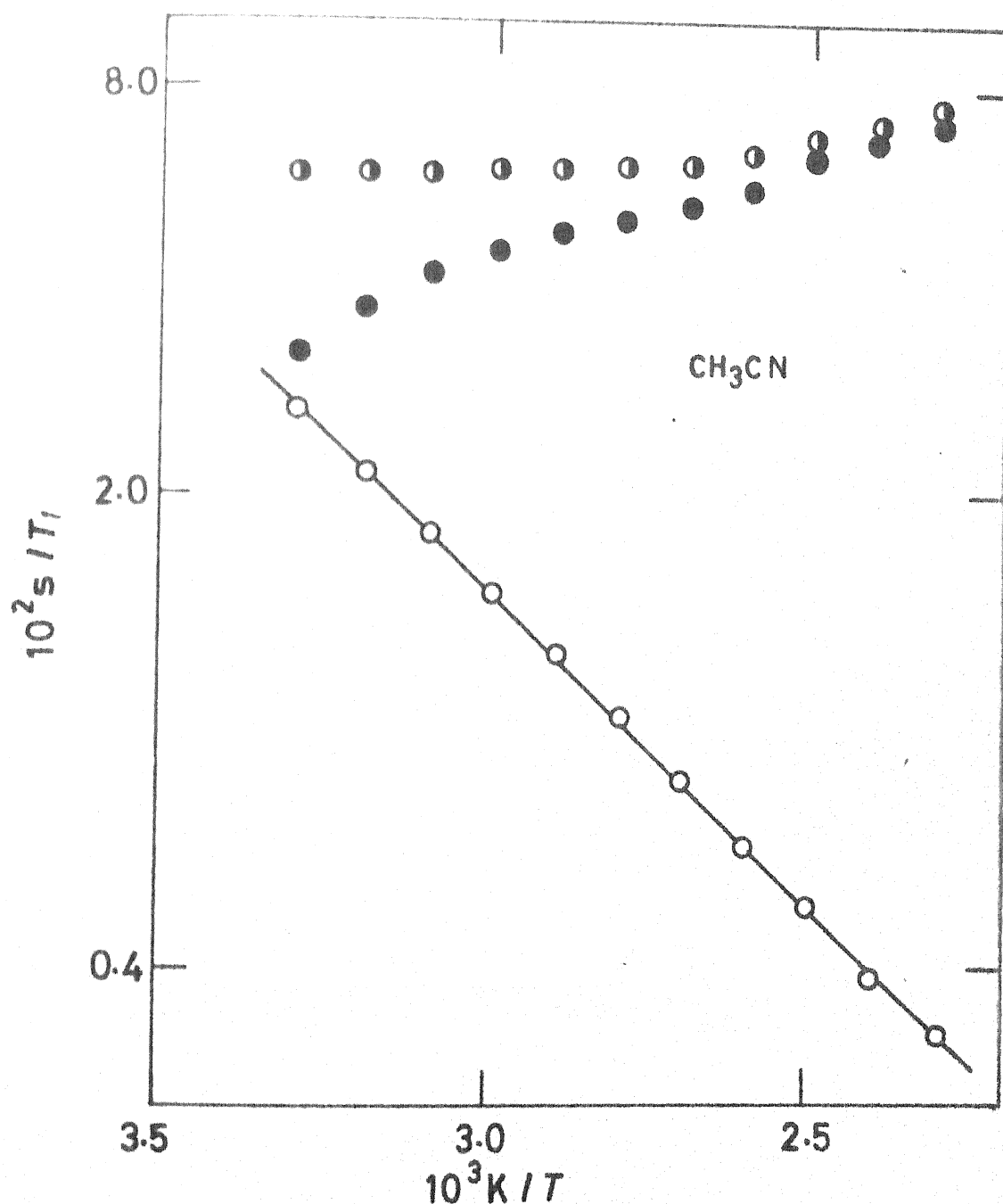
FIGURE 23 . PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES
WITH TEMPERATURE IN ACETONITRILE. ◖ , TOTAL RELAXATION
RATE (OBSERVED). ○ , INTERMOLECULAR RELAXATION RATE
(CALCULATED). ● , INTRAMOLECULAR RELAXATION RATE.
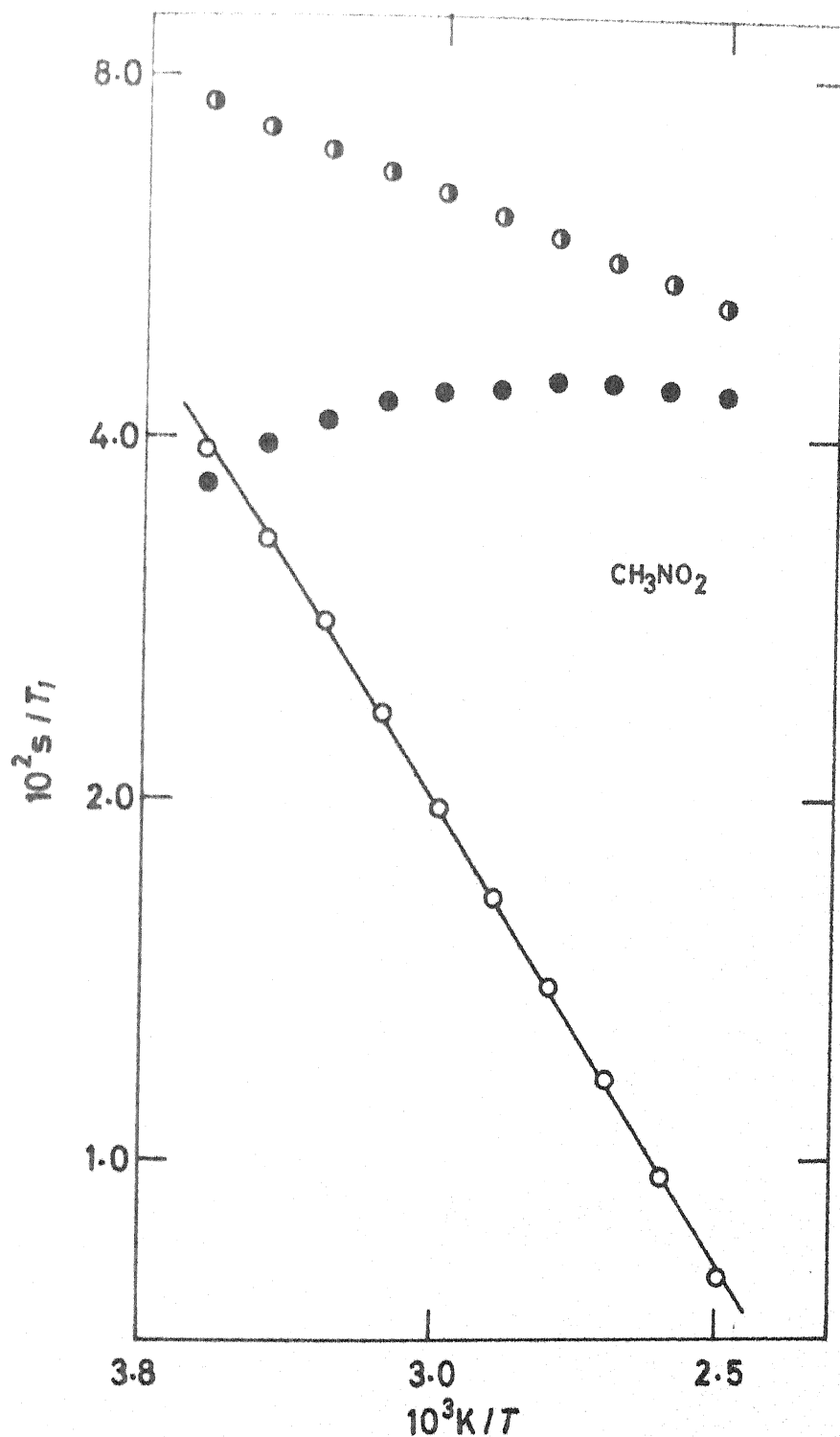
FIGURE 24. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION
RATES WITH TEMPERATURE IN NITROMETHANE. ◐ , TOTAL
RELAXATION RATE (OBSERVED). ○ , INTERMOLECULAR
RELAXATION RATE (CALCULATED). ● , INTRAMOLECULAR
RELAXATION RATE.
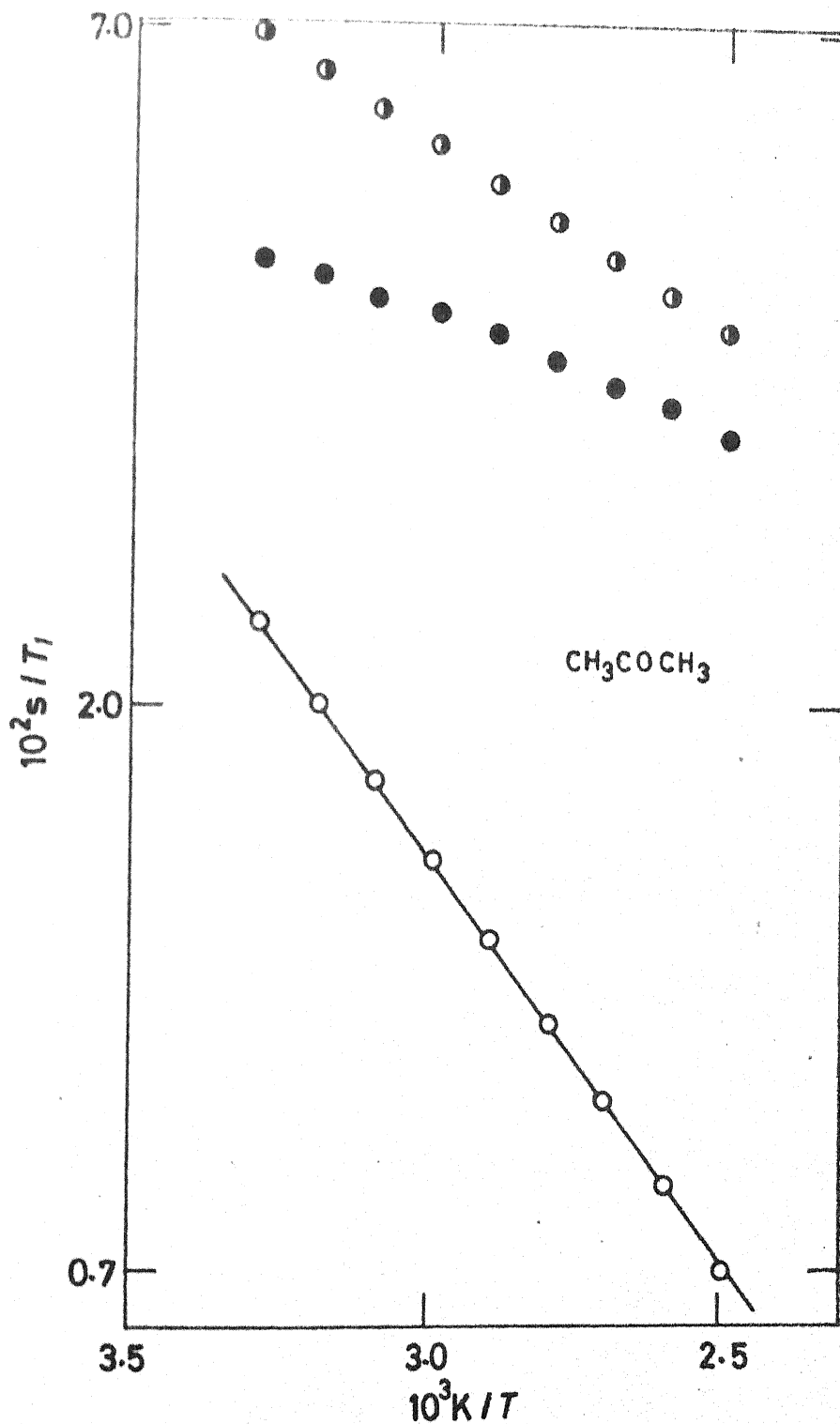
FIGURE 25. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN ACETONE. ◐ , TOTAL RELAXATION RATE (OBSERVED). ○ , INTERMOLECULAR RELAXATION RATE (CALCULATED). ● , INTRAMOLECULAR RELAXATION RATE.
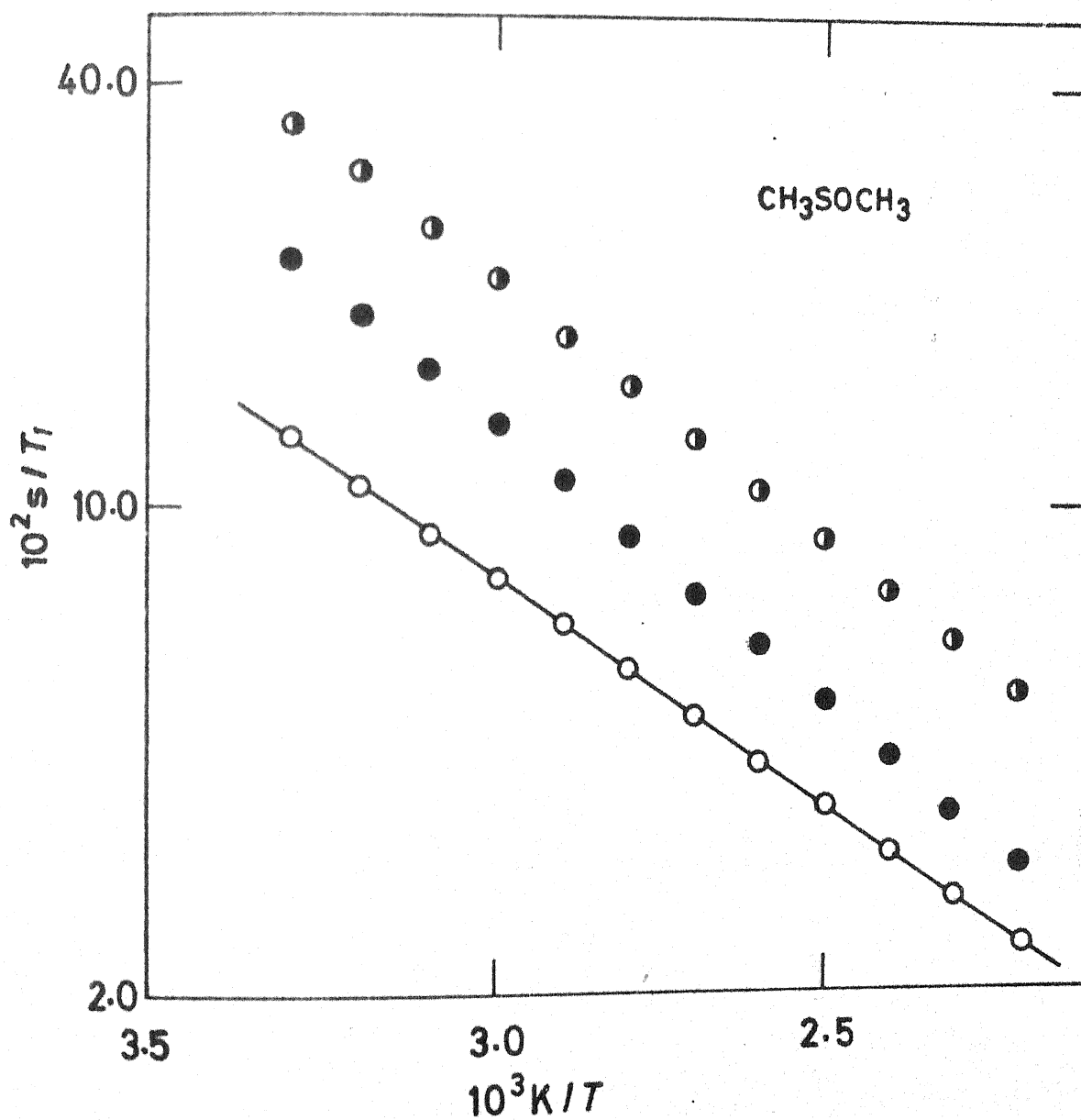
FIGURE 26. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN DIMETHYL SULFOXIDE. ◑ , TOTAL RELAXATION RATE (OBSERVED). ○ , INTERMOLECULAR RELAXATION RATE (CALCULATED). ● , INTRAMOLECULAR RELAXATION RATE.

interaction is very steeply dependent on the spin separation
(Eqs. 1.13 and 4.2) and as the distance between two spins
belonging to the different methyl groups in acetone and dimethyl
sulfoxide are quite far apart compared to the proton-proton
separation within a group (1.78Å), intramolecular interaction is
mainly confined to the interaction within a methyl group. Thus,
all the compounds presently under study behave like 3-spin
systems and the relation connecting the total intramolecular
relaxation rate to the effective correlation time $\tau_{\theta 2 \, eff}$ is
(Abragam (1961)),

$$(1/T_1)_{intra} = 3\gamma^4 \hbar^2 / r^6 \; \tau_{\theta 2 \, eff} . \qquad (4.2)$$

The plots of the effective correlation times against temperature
are given in Fig. 27. The plot for dimethyl sulfoxide is
reminiscent of the outcome of a collision limited process (see
p. 41). The slow variation of acetone $\tau_{\theta 2 \, eff}$ with temperature
is akin to the inertial reorientational motion discussed in
Chapter 3 (p. 95).

Before embarking on the discussion about the individual
compounds, it is worthwhile checking on the temperature variation
of some parameters obtained combining T_1, D, η and ρ
which could also project a rough picture of the molecular
dynamics in the liquid state in the following manner.

η: The viscosity coefficient is an outcome of the
linear momentum transfer and hence, like the velocity dependent
self-diffusion coefficient, is an attribute of the linear motion
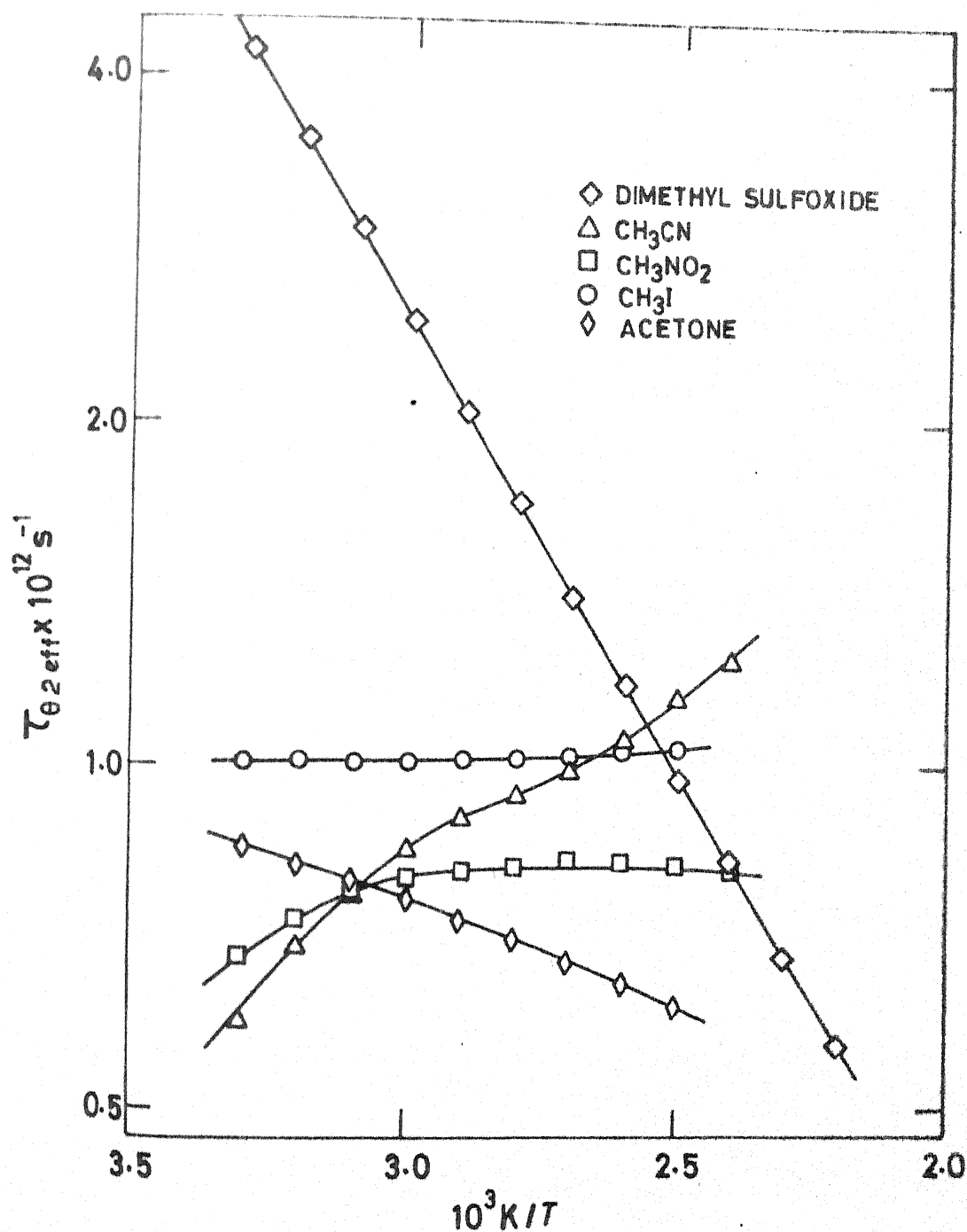
FIGURE 27. PLOTS OF THE VARIATION OF $\tau_{\theta2\,eff}$, THE EFFECTIVE REORIEN-
TATIONAL CORRELATION TIMES, WITH TEMPERATURE OF THE VARIOUS
COMPOUNDS STUDIED.

of the molecules. Therefore the comparison of the corresponding activation energies (Table 4.1) will be revealing.

$\rho/\mathcal{D}$: In Torrey's relation (Eq. 1.10) the intermolecular relaxation rate is proportional to $\rho/\mathcal{D}$. The variation of $\rho/\mathcal{D}$ with temperature is expected to be similar to the intermolecular relaxation rate and in experiments where the intermolecular relaxation rate is determined from the dilution studies in their isotopic analogues such a comparison will be illuminating. All these compounds under study have an Arrheniuslike $\rho/\mathcal{D}$ variation and the activation energies are given in Table 4.1.

$\eta\rho/T$: When the Stokes-Einstein relation is valid $(1/T_1)_{inter}$, $\rho/\mathcal{D}$ and $\eta\rho/T$ are all proportional to each other (Eqs. 11 and 12). This premise can also be tested by independent observation of the variation of $\eta\rho/T$ and $\rho/\mathcal{D}$ with temperature. So far as the trustworthiness of the two relations is concerned the Torrey's relation (comprising $\rho/\mathcal{D}$) seems to be direct, accurate and involves $\mathcal{D}$ which is measured quite accurately *in situ*. The activation energies for $\eta\rho/T$ variation with temperature are given in Table 4.1.

T/η: When the Brownian diffusion is valid for the reorientational motion the rotational diffusion coefficient ($\mathcal{D}_{rot}$) will be proportional to T/η (Eqs. 1.14, 1.17 and 1.19). It is also realized that the reorientational motion about an axis perpendicular to the molecular symmetry axis is diffusive, and hence $\mathcal{D}_\perp$ the corresponding rotational diffusion

coefficient is determined by T/η (Bopp (1967), Woessner, Snowden and Strom (1968), Gillen, Schwartz and Noggle (1971), Lyerla, Grant and Wang (1971), and Heatley (1974)). The corresponding activation energies are given in Table 4.1.

$\eta/T\rho$: In the event of rotational Brownian motion and absence of spin-rotation interaction of any consequence the intramolecular dipolar relaxation rate which is proportional to the reorientational correlation time gets directly related to $\eta/T\rho$ through the Debye relation (Eq. 1.11). All except dimethyl sulfoxide (where the activation energy is found to be temperature dependent), have well defined activation energies as presented in Table 4.1.

There are some other derived parameters which are also of interest:

$T_1\eta\rho/T$: The initial suggestion by Blicharski that a decreasing $T_1\eta\rho/T$ with temperature increase suggests the presence of sizeable spin-rotation interaction was later shown to be due to convection currents in the experimental sample (Kosfeld (1968)). The observation in the present series of compounds does not show any appreciable decrease of $T_1\eta\rho/T$ with temperature rise - except in CH_3CN where it is fairly big.

$\eta T_1/T$: Hydrogen bondings seem to sharply decrease $\eta T_1/T$ with temperature rise (Hennel and Waluga (1962)).

increases from $3.55 \times 10^9 m^{-2} s$ to $4.71 \times 10^9 m^{-2} s$) suggesting distinctive diffusive process governing the relaxation.

The Table 4.2 carries the following informations at the upper and lower temperature limits of the experiments. It has the effective correlation time $\tau_{\theta 2}$ **eff** defined by the Eq. 4.2 and the Bloembergen-Purcell-Pound correlation time $\tau_{\theta 2}$ BPP as determined by Eq. 1.11 and the Stokes-Einstein radius from the Table App. 2. The maximum value of the reorientational correlation time in the Gaussian or inertial limit (Inertial $\tau_{\theta 2}$ av) as given by Eq. 1.20 is also presented. The molecular free rotational time (Bartoli and Litovitz (1972), Bauer, Brauman and Pecora (1974), Fury and Jonas (1976))

$$\tau_{\text{free av}} = 2\pi/9 \ \sqrt{I_{av}/kT} \qquad (4.5)$$

(where I_{av} is the average moment of inertia of the molecule defined by

$$I_{av} = 3(I_A^{-1} + I_B^{-1} + I_C^{-1})^{-1})$$

is also presented in Table 4.2. The reorientational correlation time (Mod. Hill $\tau_{\theta 2 \ av}$) obtained using the modified Hill relation (see, Hill (1954), Mitchell and Eisner (1960), Assink and Jonas (1969), and Pajak *et al* (1970))

$$\tau_{\theta 2} = 2\sigma I_{av} \eta/mkT , \qquad (4.6)$$

where σ the average of the semi axes of the molecule in the

TABLE 4.2

THE CORRELATION TIMES IN THE METHYL GROUP CONTAINING COMPOUNDS

Compound	$10^3 K/T$	$\tau_{\theta 2}$ eff $\times 10^{13} s^{-1}$	$\tau_{\theta 2}$ BPP $\times 10^{13} s^{-1}$	τ_{free} av $\times 10^{13} s^{-1}$	Inertial $\tau_{\theta 2}$ av $\times 10^{13} s^{-1}$	Mod. Hill $\tau_{\theta 2}$ av $\times 10^{13} s^{-1}$
$CH_3 I$	3.3	10.60	12.17	1.32	0.97	0.19
	2.5	13.80	4.90	1.15	0.84	0.08
$CH_3 CN$	3.3	5.99	2.56	1.31	0.96	0.32
	2.3	13.20	0.72	1.09	0.80	0.09
$CH_3 NO_2$	3.4	6.81	26.03	3.19	2.34	4.22
	2.5	8.06	7.30	2.73	2.00	1.19
$CH_3 COCH_3$	3.3	8.52	11.63	2.74	2.01	1.50
	2.5	6.16	4.07	2.38	1.75	0.53
$CH_3 SOCH_3$	3.3	42.11	117.97	4.02	2.95	18.60
	2.2	5.70	17.97	3.28	2.41	2.83

present calculation is taken to be the Stokes-Einstein radius, m is the mass of the molecule and others have their usual meaning. The total intramolecular relaxation rate, the Bloembergen-Purcell-Pound intramolecular dipolar relaxation rate, and the maximum intramolecular relaxation rate expected in the event of a Gaussian (inertial) reorientation (Moniz, Steele and Dixon (1963)), bear the same ratio to one another as the corresponding correlation times. The effective χ parameter defined by

$$\chi_{eff} = \tau_{\theta 2 \ eff} / \tau_{free}$$

is presented in Table 4.3.

The parameter $a_2^m(0)$ defined by Moniz, Steele and Dixon (1963) as

$$a_2^m(0) = \tau_{\theta 2 \ eff} \sqrt{kT/I} \qquad (4.7)$$

in the inertial limit becomes $a_2^m(0) = 1/2 \sqrt{\pi/3} \approx 0.5$, and in the diffusion limit yields

$$a_2^m(0) = \xi/6\sqrt{IkT} . \qquad (4.8)$$

$a_2^m(0) \ (= a_2^m(0)_{eff})$ determined using Eq. 4.7, and the other $a_2^m(0) \ (= a_2^m(0)_{av})$ obtained using Eq. 4.8 are presented in the Table 4.3. $a_2^m(0)_{av}$ bears the following relation to the χ parameter in the Debye diffusion limit, and the ratio of the intramolecular dipolar relaxation rate (estimated by Bloembergen, Purcell and Pound relation) to the relaxation rate in the Gaussian (inertial)

TABLE 4.3

SOME MOLECULAR PARAMETERS IN THE METHYL GROUP CONTAINING COMPOUNDS

Compound	$10^3 K/T$	χ_{eff}	$a_2^m(0)_{eff}$	$a_2^m(0)_{av}$	Dipole moment D^{-1}
CH_3I	3.3	8.0	5.59	6.4	1.48
	2.5	11.5	8.37	3.0	
CH_3CN	3.3	4.6	3.19	1.4	3.39
	2.3	12.1	8.43	0.5	
CH_3NO_2	3.4	2.1	1.49	5.7	4.39
	2.5	2.9	2.06	1.9	
CH_3COCH_3	3.3	3.1	2.17	3.0	2.93
	2.5	2.6	1.81	1.2	
CH_3SOCH_3	3.3	10.5	7.31	20.5	3.9
	2.2	1.7	1.21	3.8	

limits are

$$X_{Debye} = 9/2\pi \quad a_2^m(0)_{av} \quad ,$$

and $R_{1rot\ BPP}/R_{1rot\ Gaussian} = 2\sqrt{3/\pi}\ a_2^m(0)_{av}.$

The dipole moments of the investigated molecules (McClellan (1963)) are also given in Table 4.3.

4.1 CH_3I and CH_3CN

These two symmetric top molecules have been subjected to a large number of rotational and vibrational spectroscopic studies (Favelukes *et al* (1968), Rothschild (1969, 1970a, 1970b), Constant (1973a, 1973b), Griffiths (1973, 1974), Wright, Schwartz and Wang (1973), Yarwood (1973)). In nmr work the symmetric tops, being of next higher degree of complication than the spherical tops have proved to be the testing ground for the models for anisotropic rotational motion (Moniz and Gutowsky (1963), Zeidler (1965), Bopp (1967), Woessner, Snowden and Strom (1968), Bull and Jonas (1970), Franck, Hertz and Rädle (1970), Gillen, Schwartz and Noggle (1971), Lyerla, Grant and Wang (1971), Heatley (1974), Leipert, Noggle and Gillen (1974)).

The CH_3I $E(\mathcal{D}) = 2.41$ kcal/mole obtained in the present work (Table 4.1) compares favourably with the results of Krüger and Weiss (1970) 2.0 kcal/mole and that of Sandhu (1975a) 2.11 kcal/mole. The intermolecular relaxation rate estimated using the Torrey's relation (Eq. 1.10) compares well with the corresponding values obtained *via* dilution study (Gillen, Schwartz and Noggle (1971)) and the respective activation

energies (2.75 kcal/mole and 2.4 kcal/mole) are quite close.
Even though the separation of the intramolecular dipolar and
spin-rotation relaxation rates could not be done the slow varia-
tion of the intramolecular relaxation rate in CH_3I and CH_3CN
(Figs. 22 & 23) are indicative of coherent reorientational motion
(p. 95). The close agreement between the $\tau_{\theta_2\ BPP}$ and $\tau_{\theta_2\ eff}$ in
Table 4.2 is misleading because of the following reasons. $\tau_{\theta_2\ BPP}$
estimates are usually large because of not taking into account
the inertial effects (Moniz, Steele and Dixon (1963)) and $\tau_{\theta_2\ eff}$
estimated here is larger than the reorientational correlation time
because of the inclusion of large spin-rotation interaction contri-
bution. Hence the present close agreement in no way suggests the
validity of the diffusional model. Also because of the large contri-
bution of spin-rotation interaction to the value of the effective
rotational correlation time, the χ_{eff} presented in Table 4.3 is
also large, and seems to increase with temperature.

In CH_3CN the variation of the self-diffusion coefficient with
temperature seems to be very fast. The $E(\mathcal{D}) = 3.65$ kcal/mole (Table
4.1) obtained here is much larger than the value 2.63 kcal/mole
reported by Zeidler (1971b). The variation of the coefficient of
viscosity (η) with temperature is comparatively much slower
($E(\eta) = 1.83$ kcal/mole in Table 4.1) and therefore gives a $\mathcal{D}\eta/T$
increasing quite fast in the experimental temperature range (Table
App. 1). This leads to a higher average $\mathcal{D}\eta/T$ value and a
consequent smaller Stokes-Einstein radius (see p.178). As a
consequence of the large $\mathcal{D}$ variation, the $\rho/\mathcal{D}$ variation with

temperature is also quite fast, thus giving $E(\rho/\mathcal{D}) = 4.26$ kcal/mole (Table 4.1) which is much larger than the corresponding values, 2.0 kcal/mole reported by Woessner, Snowden and Strom (1968) and 2.2 kcal/mole reported by Gillen et al (1972). As mentioned in p.119 the rapid decrease of $T_1 \eta \rho/T$ with temperature rise probably suggests the presence of convection currents in the sample.

There is a growing feeling (Bopp (1967), Woessner, Snowden and Strom (1968), Gillen, Schwartz and Noggle (1971), Lyerla, Grant and Wang (1971), and Heatley (1974)), that in the symmetric top molecules presently under consideration, the rotational diffusion about an axis parallel to the molecular symmetry axis is free inertial and that about an axis perpendicular to the symmetry axis is diffusional. We present in the following the corresponding estimated (Eqs. A.9, 1.11 and 4.5) rotational diffusion constants and those values presented by others. The values obtained with the assumption that the CH_3CN molecular radius is at least equal to the CH_3I Stokes-Einstein radius, are also presented.

Compound	$10^3 K/T$	Calculated $\mathcal{D}_{\perp} \times 10^{-11}s$	Calculated $\mathcal{D}_{,,} \times 10^{-11}s$
CH_3I	3.3	1.37	20.8
	2.5	3.39	23.9
CH_3CN	3.3	6.5	20.8
	2.3	23.08	23.9
	3.3	1.80	20.8
	2.3	6.40	23.9

(In the preceding tabulation the third and fourth rows correspond to a_{SE} = 0.90 Å and the fifth and sixth rows correspond to a_{SE} = 1.38 Å.) The $D_\perp$ and $D_{,,}$ values reported by others are as follows. In CH_3I :

Author(s)	$D_\perp \times 10_\perp^{-11}$s	$D_{,,} \times 10^{-11}$s
Gillen, Schwartz and Noggle (1971)	1.17	-
Griffiths (1973)	1.07	-
Heatley (1974)	1.1	13.2
Lyerla and Levy (1974)	1.4	20.0

In CH_3CN:

Author(s)	$D_\perp \times 10^{-11}$s	$D_{,,} \times 10^{-11}$s
Bopp (1967)	1.35	12.0
Zeidler (1971b)	1.4	12.0
Griffiths (1973)	1.51	-
Heatley (1974)	1.7	16.32
Lyerla and Levy (1974)	1.5	14.0

In CH_3CN, at $10^3K/T$ = 3.3, χ is small (Table (4.2) and the reorientation is nearly inertial. $a_2^m(0)$ seem also to be both theoretically and experimentally over-estimated although at $10^3K/T$ = 2.3 $a_2^m(0)_{av}$ = 0.5 indicates Gaussian reorientational situation.

4.2 CH_3NO_2

Nitromethane has a very small barrier to internal rotation (p. 97), a large dipole moment (Table 4.3), and a normal boiling point (100.8 ^{o}C) close to that of water. An early work by Anderson (1969) had shown that even in liquid nitromethane $T_1 \neq T_2$. Tyn and Calus (1975) find such olefinic derivatives as CH_3NO_2 to be quite unpredictable whose molar volumes could not be easily ascertained. All these *prima facie* make liquid CH_3NO_2 quite interesting to work on.

In the D measurement instead of plotting log $S(0)/S_z$ *vs* t^3 as stated in p. 81, $1/t$ log $S(0)/S_z$ *vs* t^2 are plotted to get D from the slope and keep D measurement immune from the 'effect of T_2'. Since T_2 is of the order of a few seconds (but not very small where such T_2 effects are hazardous) such a precautionary step seems to be in the conservative side. Our $E(D) = 3.02$ kcal/mole can be compared with the following results: 3.8 kcal/mole obtained by McCall *et al* (1959) and 2.53 kcal/mole obtained by O'Reilly *et al* (1971). As against Pendred, Pritchard and Richards (1966) reported value of T_1 (12.7 s) the value obtained presently is 13.9 s. The small variation of T_1 (Fig. 16) over the experimental temperature range suggests pre-eminence of the inertial motion which is further corroborated by the slow variation of the intramolecular relaxation rate with temperature (Fig. 24). The intramolecular relaxation rate which is of about the same magnitude as the intermolecular relaxation rate at the room

temperature becomes about five times larger at 127 $^{\circ}$C indicating good deal of rotational coherence (Chap. 3). This is interesting as CH_3NO_2 being highly polar would give a local structure which does not seem to affect the rotational motion. This also corroborates the earlier realization that molecular shape but not the dipole moment governs the reorientational motion (see p. 43).

In Table 4.3 the low χ_{eff} , around 2.5 is suggestive of a good deal of inertial motion. Modified Hill method with accent on the reorientational motion seems to predict $\tau_{\theta 2}$ well in CH_3NO_2 at room temperature. The calculated overall rotational diffusion constant is given in the Appendix (Table App. 3).

4.3 CH_3COCH_3 and CH_3SOCH_3

These two molecules although structurally similar, dimethyl sulfoxide has a higher barrier to internal rotation (2.2 kcal/mole) than acetone (0.778 kcal/mole as in p. 97, and 0.92 kcal/mole as obtained by Lyerla and Levy (1974)), and as the methyl groups within each molecule are far apart these molecules essentially behave as three spin systems so far as the calculation of intramolecular interaction is concerned. Dimethyl sulfoxide is highly hygroscopic, acts as a good solvent, and seems to be of great physiological importance. The dimethyl sulfoxide molecule has a large dipole moment (3.9D) and interestingly enough has normal melting point (18.45 $^{\circ}$C) close to the room temperature.

In acetone, the $E(D) = 2.58$ kcal/mole (Table 4.1) can be compared with the following values obtained by others: 2.03 kcal/mole McCall *et al* (1959), 2.1 kcal/mole Krüger and Weiss (1970). In acetone the present finding $E(R_1 \text{ total}) = 1.35$ kcal/mole compares well with 1.5 kcal/mole obtained by Bonera and Rigamonti (1965). As discussed in Chapter 3 the slow variation of the intramolecular relaxation rate in acetone (Fig. 25) might indicate dominant surrounding independent intramolecular rotational contribution to relaxation. This looks feasible as the acetone being fairly asymmetric in shape, the overall rotational coherence in the experimental temperature range looks improbable. The small χ values for acetone in Table 4.3 also hints at possible inertial rotational motion. The $\tau_{\theta_2 \text{ eff}}$ plot in Fig. 27 when fitted to an Arrhenius relation gives $E(\tau_{\theta_2 \text{eff}}) = 0.8$ kcal/mole which is fairly close to an approximate evaluation: $E(T^{1}/^{2}) = 0.37$ kcal/mole in $10^3 K/T$ range 3.3 to 2.2. As discussed in Chap. 3 this is suggestive of a reorientational coherence in acetone over the present experimental temperature range which bears out the *prima facie* observation that the internal rotation barrier being low, the experimental temperature range will sufficiently activate the internal rotation.

The most significant observation in dimethyl sulfoxide is the fast and almost similar variation of the total, inter- and intramolecular relaxation rates with temperature (Fig. 26). (To be exact, the plots show the translational motion slightly more

facile than the overall rotational motion.) Since the fast

decrease of intramolecular relaxation rate with temperature

rules out any reckonable spin-rotation interaction contribution

to relaxation the $\tau_{\theta 2 \ eff}$ is a measure of the dipolar correlation

time. The Arrheniuslike variation of the reorientational corre-

lation time could suggest a collision limited diffusive process

governing the reorientational process. The similar variation

of the intermolecular and intramolecular relaxation rates would

then mean that the translational and reorientational process are

well coupled. Since dimethyl sulfoxide looks structurally

asymmetric and the internal rotational barrier is large such an

observation looks quite tenable. However, with increase of

temperature χ seems to suggest a transition from the diffusion

to an inertial limit.

The chemists are a hardy lot.

CHAPTER 5

STUDIES IN A GROUP OF ASSORTED MOLECULAR LIQUIDS

Investigations into the molecular motion in a group of assorted compounds (methylene chloride (CH_2Cl_2), methylene iodide (CH_2I_2), anisole ($C_6H_5OCH_3$), and α-trifluoro toluene ($C_6H_5CF_3$)) are reported in the present chapter. In the temperature range of the experiment (300 to 450 K) the barrier to internal rotation of the CF_3 group about the $C-CF_3$ bond is 0.2 to 0.4 kcal/mole (Bull, Barthell and Jonas (1971)), which is easily surmounted and a good amount of internal rotation is possible. As ^{19}F has characteristically a large spin-rotation coupling constant, one expects large spin-rotation interaction contribution to ^{19}F relaxation.

Some other general observations on these molecules are as in the following. Anisole is a bent molecule with the $C-O-CH_3$ angle ~ 108°. The C_6H_5 and CH_3 protons in anisole are expected to be chemically shifted from one another to give cross-relaxation effects in the observation of the ^1H overall relaxation. The overall molecular asymmetry is a common feature of the present group of compounds. The moments of inertia about the principal molecular axes available for all except anisole, are as follows.

Compound	$I_A \times 10^{47}$ kg^{-1} m^{-2}	$I_B \times 10^{47}$ kg^{-1} m^{-2}	$I_C \times 10^{47}$ kg^{-1} m^{-2}	Source of data
CH_2Cl_2	26.3	253.0	278.0	Myers and Gwinn (1952)
CH_2I_2	37.4	1345.0	1377.0	Sandhu et al (1976)
$C_6H_5CF_3$	295	886.83	1035.26	Ogata and Cox (1976)

Apart from the large asymmetry in the moment of inertia about different axes in CH_2Cl_2 and CH_2I_2 it is also noticed that CH_2Cl_2 ($M_r = 84.94$) is much lighter than CH_2I_2 ($M_r = 267.87$), and therefore it is expected that in these two structurally similar molecules mass dependent dynamical properties might be discerned.

The molecular structural asymmetry of these compounds *a priori* suggests good translation-rotation coupling, which results in the similar variation of the intermolecular and intramolecular dipolar relaxation rates, and an overall diffusive reorientational motion.

T_1 and D measured over suitable temperature ranges in these compounds are shown in Figs. 28 to 35. At the out set the rapid variation of the proton T_1 with temperature suggests that the relaxation is governed by surrounding dependent diffusive processes which are much more temperature sensitive than the inertial processes. The self-diffusion coefficients fit into an Arrhenius type relation whose activation energies are given in Table 5.1 (See also comments on p. 99.)
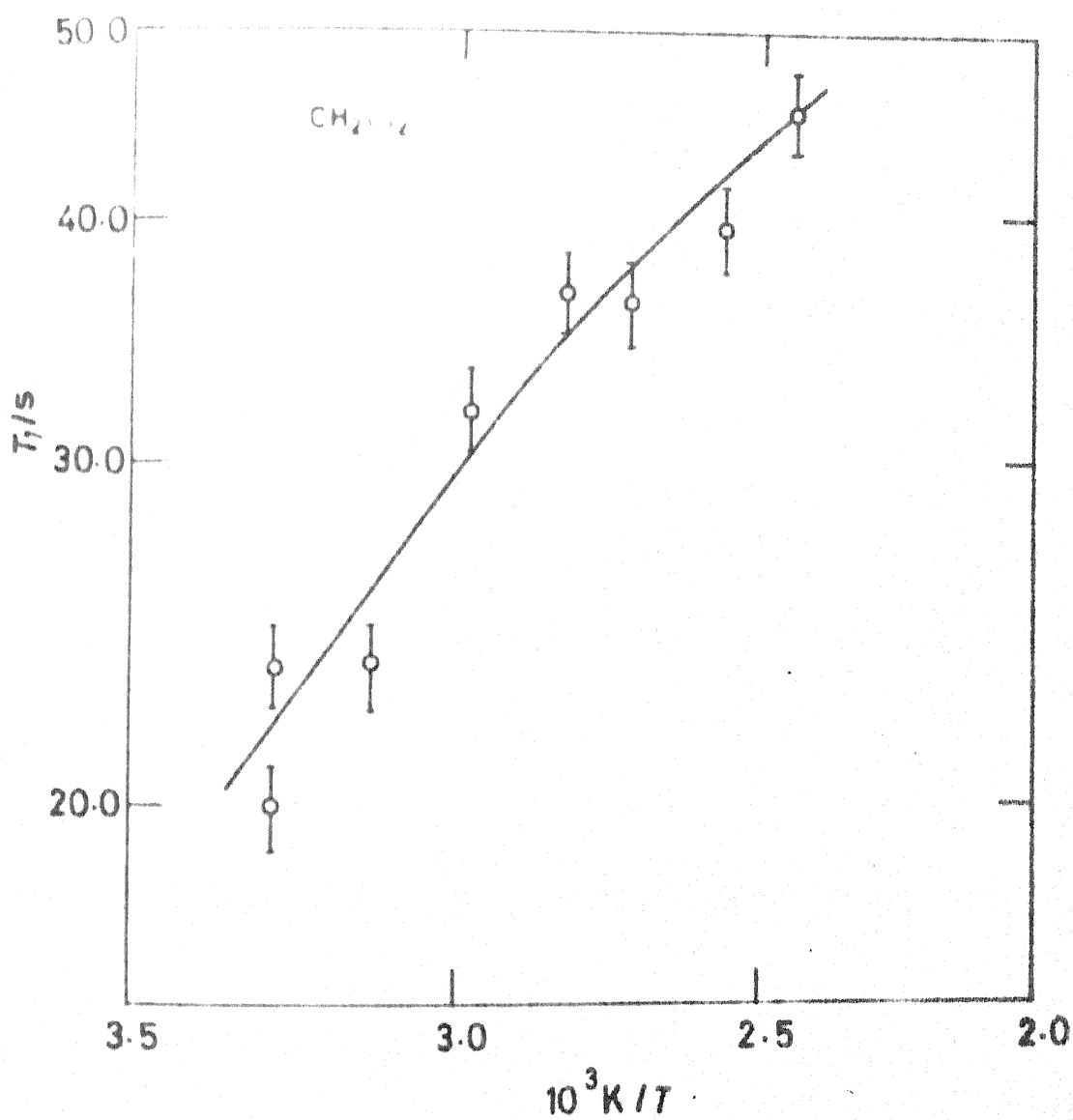
FIGURE 28 . TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T₁) IN METHYLENE CHLORIDE.
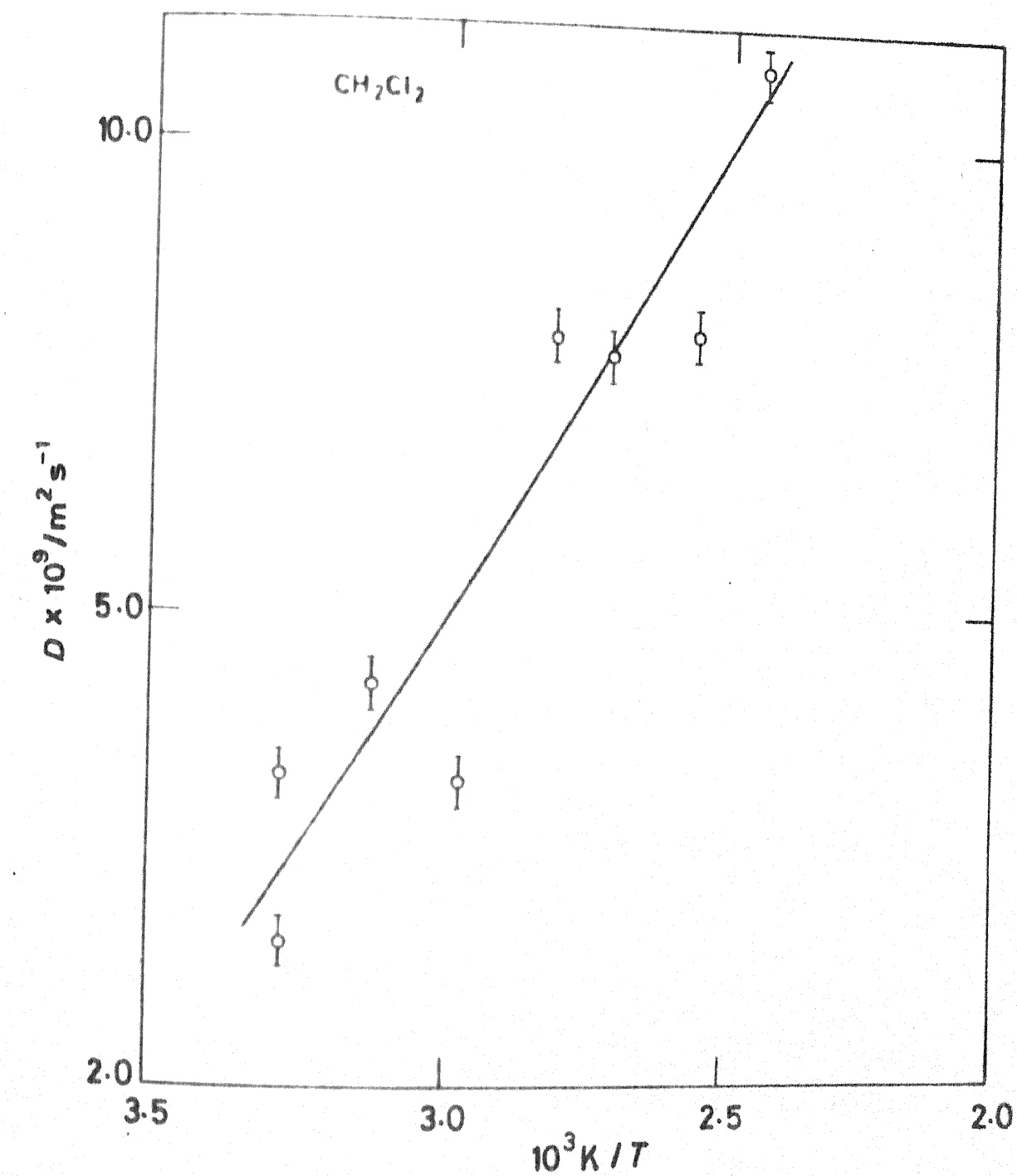
FIGURE 29. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN METHYLENE CHLORIDE.
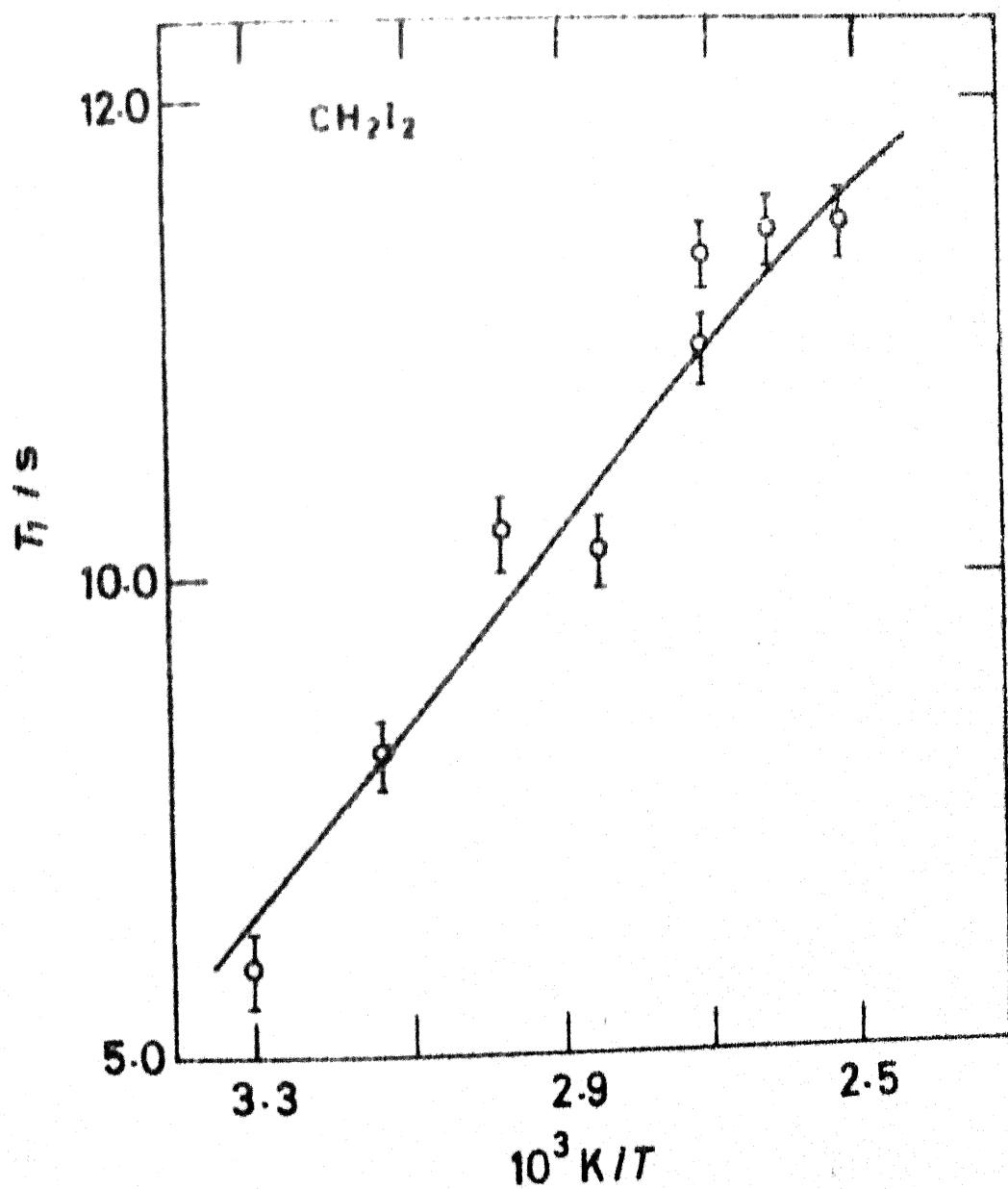
FIGURE 30. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) IN METHYLENE IODIDE.
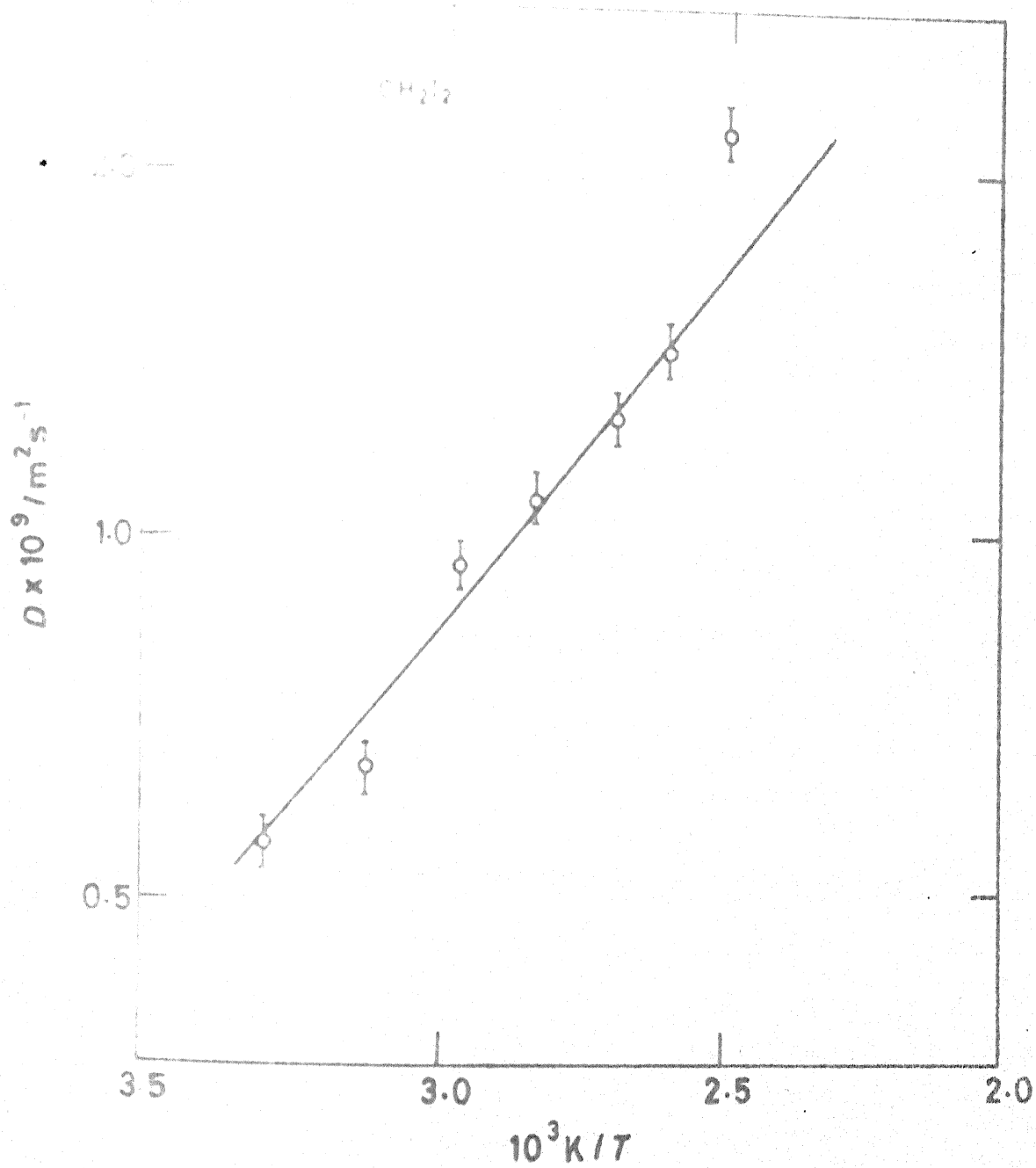
FIGURE 31. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN METHYLENE IODIDE.
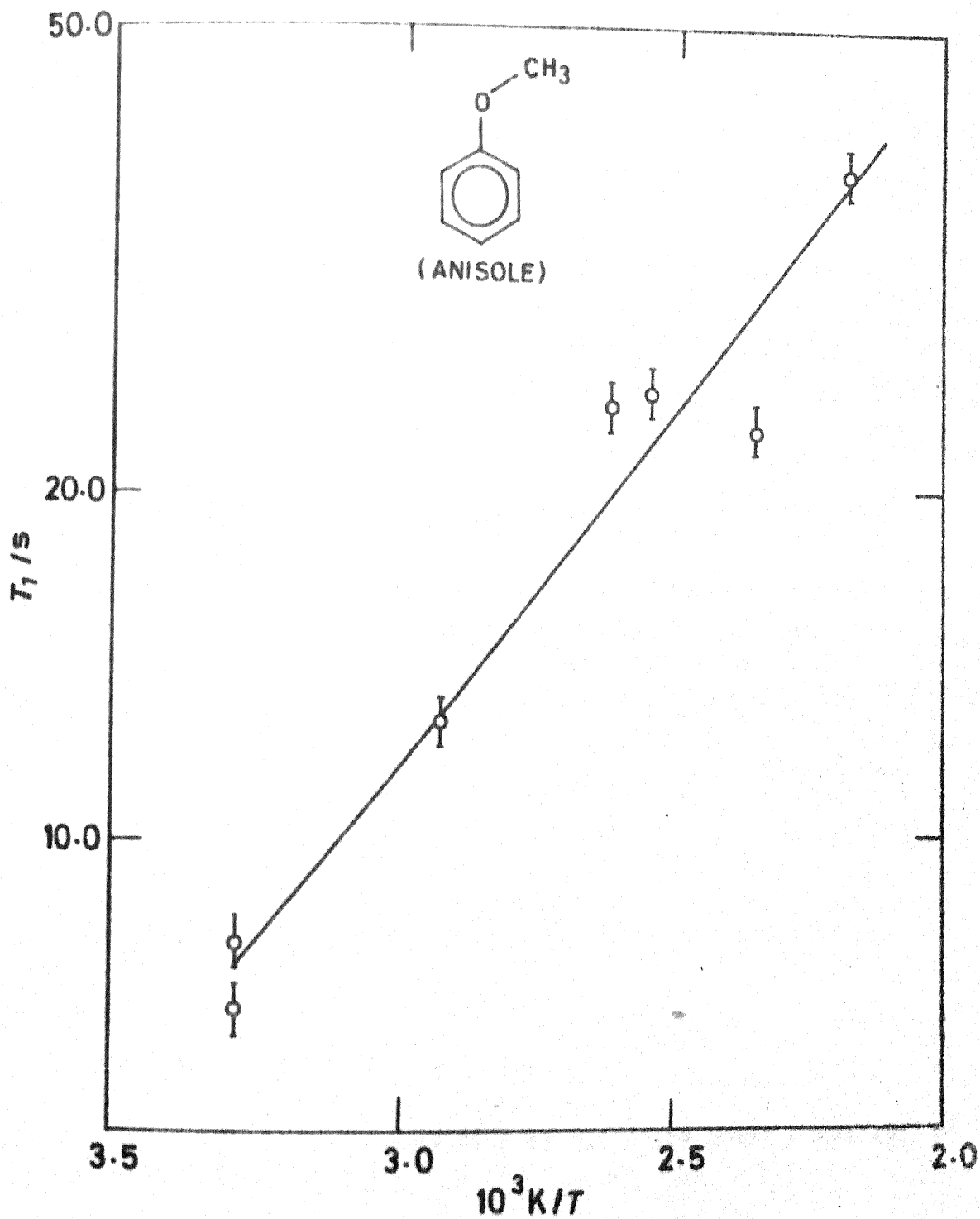
FIGURE 32. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME (T_1) IN ANISOLE.
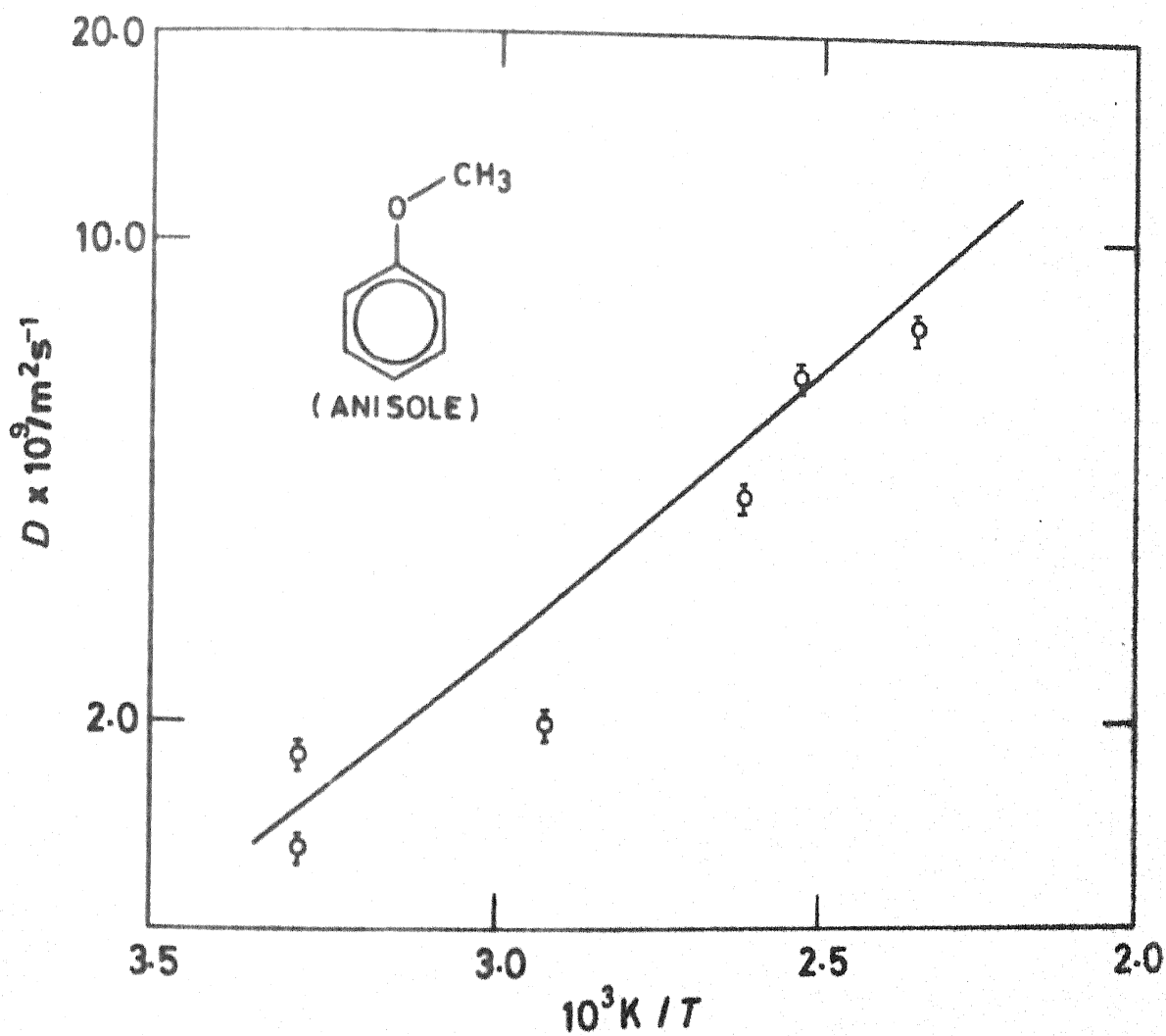
FIGURE 33. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN ANISOLE.
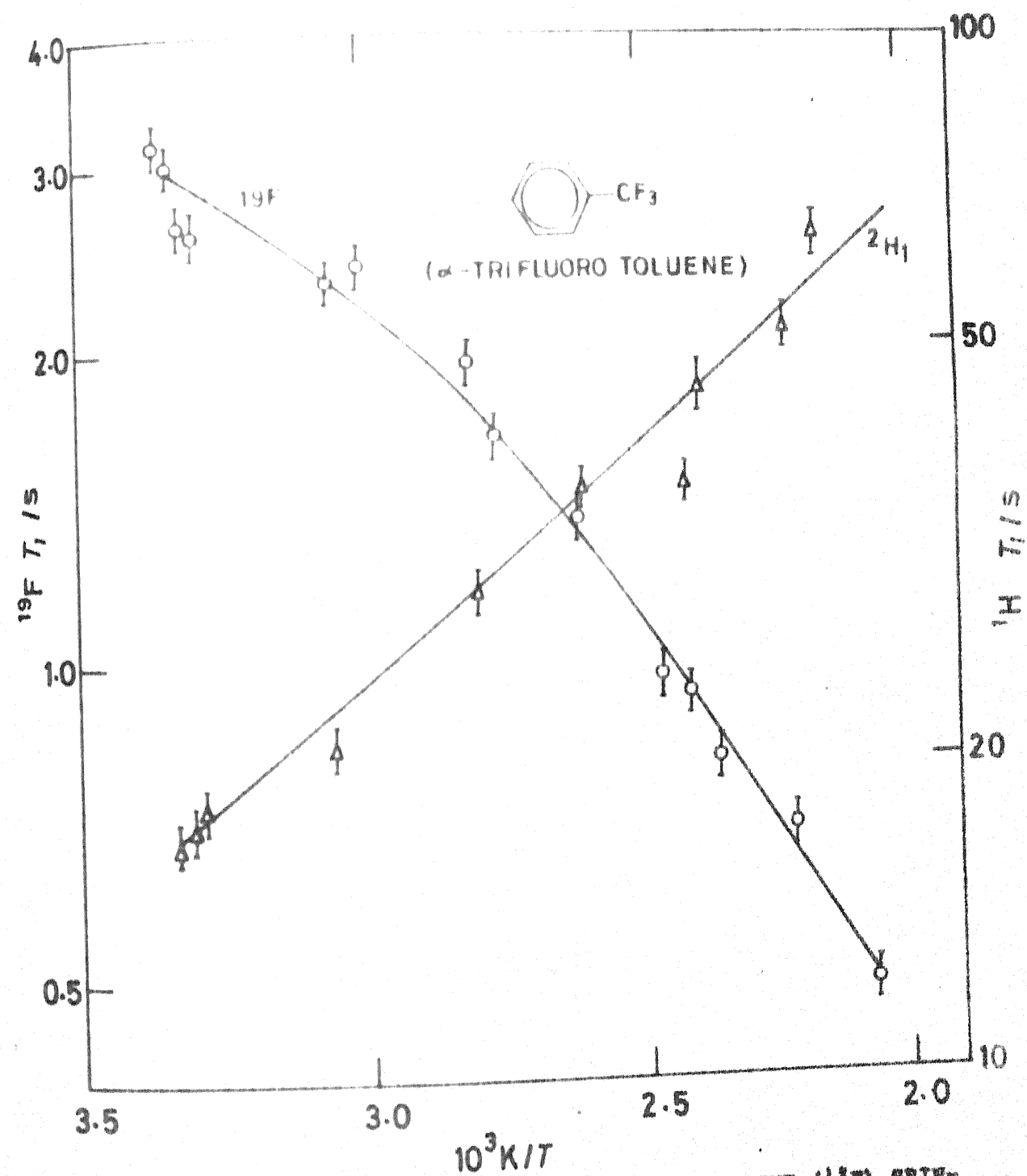
FIGURE 34. TEMPERATURE DEPENDENCE OF PROTON (^{1}H) AND FLUORINE (^{19}F) SPIN-LATTICE RELAXATION TIME (T_1) IN α-TRIFLUORO TOLUENE.
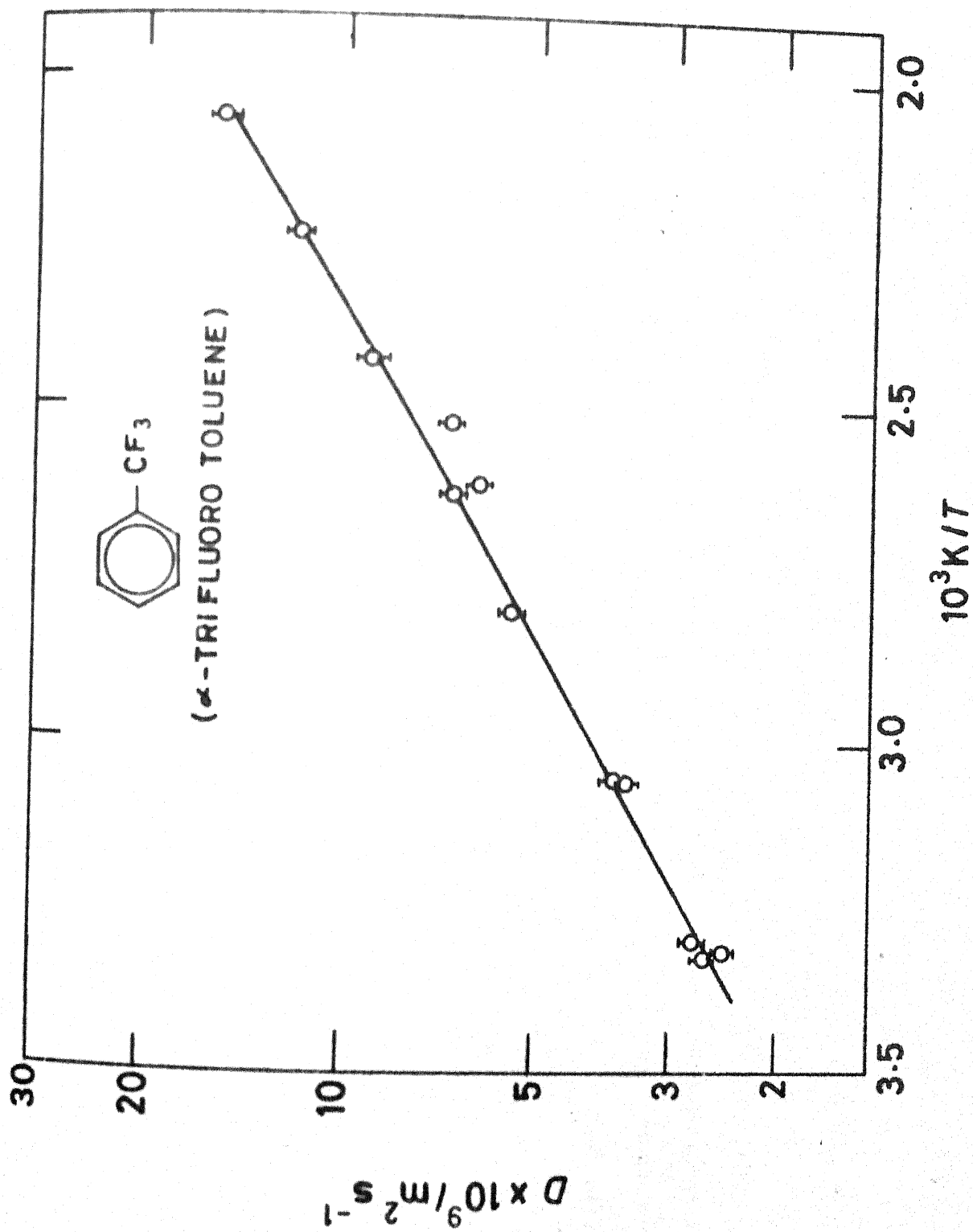
FIGURE 35. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENT (D) IN α-TRIFLUORO TOLUENE.

TABLE 5.1

THE ACTIVATION ENERGIES OF THE VARIOUS PARAMETERS IN A GROUP OF ASSORTED COMPOUNDS

Compound	$E(D)$ $(kcal)^{-1}$. mole	$E(\eta)$ $(kcal)^{-1}$. mole	$E(\rho/D)$ $(kcal)^{-1}$. mole	$E(\eta\rho/T)$ $(kcal)^{-1}$. mole	$E(T/\eta)$ $(kcal)^{-1}$. mole	$E(\eta/T\rho)$ $(kcal)^{-1}$. mole	$E(R_{1intra})$ $(kcal)^{-1}$. mole	$E(R_{1total})$ $(kcal)^{-1}$. mole
CH_2Cl_2	3.37	1.58	3.73	2.69	2.34	1.84	—	—
CH_2I_2	2.73	2.3	2.92	3.21	3.01	3.03	—	—
$C_6H_5OCH_3$	3.29	2.67	3.59	3.75	3.39	3.09	2.23	2.84
$C_6H_5CF_3$	2.77	1.89	2.86	—	—	—	1.83	2.12

$E(D)$ and $E(T/\eta)$ are obtained from the corresponding linear plots obeying $E(X) = -R \frac{\partial lnX}{\partial 1/T}$ where X stands for D and T/η and $E(\eta)$, $E(\rho/D)$, $E(\eta\rho/T)$, $E(\eta/T\rho)$, $E(R_{1intra})$, and $E(R_{1total})$ are obtained from the corresponding linear plots obeying $E(Y) = R \frac{\partial lnY}{\partial 1/T}$, where Y stands for η, ρ/D, $\eta\rho/T$, $\eta/T\rho$, R_{1intra} and R_{1total}.

The error in the activation energy calculation is about 5%.

In order to estimate the molecular radius from Stokes-Einstein relation (Eq. 1.12) and the intramolecular relaxation rate from the Torrey's relation (Eq. 1.10) the viscosity and density data necessary in the experimental temperature range are the extrapolated values taken from the following sources:

Compound	Density data available in the temperature range	Source of data
CH_2Cl_2	-30 °C to 70 °C	Landolt-Börnstein (1971a)
CH_2I_2	10 °C to 90 °C	Griffing et al (1954)
$C_6H_5OCH_3$	0 °C to 15 °C	Landolt-Börnstein (1971b)
$C_6H_5CF_3$	Only at 14 °C	Handbook of Chemistry and Physics (1962)

Compound	Viscosity data available in the temperature range	Source of data
CH_2Cl_2	-32 °C to 70 °C	Landolt-Börnstein (1969b)
CH_2I_2	30 °C to 150 °C	ibid. (1969b)
$C_6H_5OCH_3$	14.55 °C to 152.2 °C	ibid. (1969c)
$C_6H_5CF_3$	20 °C to 60 °C	ibid. (1955)

In $C_6H_5OCH_3$ and $C_6H_5CF_3$ the density data are available only in a very limited temperature range. Extrapolation over the

desired temperature range is carried out assuming that the density variation with temperature in $C_6H_5OCH_3$, $C_6H_5CF_3$ and $C_6H_5CH_3$ (toluene) are similar. The similar variation of the coefficient of viscosity with temperature in $C_6H_5CF_3$ and $C_6H_5CH_3$ adds credence to this contention. The $C_6H_5CH_3$ density data available in Vargaftik (1975) over the temperature range -100 $^\circ$C to 110 $^\circ$C are made use of.

The $D\eta/T$ values are given in Table App. 1 and the Stokes-Einstein molecular radii derived therefrom are given in Table App. 2. The total relaxation rates, the intermolecular relaxation rates obtained using the Torrey's relation (Eq. 1.10), and the total intramolecular relaxation rates as the difference between the two aforementioned relaxation rates for the compounds are plotted in Figs. 36 to 39. The corresponding activation energies, in cases wherever the stated parameters can be fitted to Arrheniuslike relation, are given in Table 5.1.

In the stated figures, attributes catching immediate attention are the following: Against our hope of fast variation of the relaxation rates in such asymmetric molecules, the slow variation of the intramolecular relaxation rate in $CH_2C\ell_2$ (Fig. 36) could be due to the facetious reorientational motion in this light molecule. Almost similar variation of the proton relaxation rates in CH_2I_2 and $C_6H_5CF_3$ implies good translation-rotation coupling quite becoming of such heavy asymmetric molecules. The ^{19}F relaxation is almost totally determined by
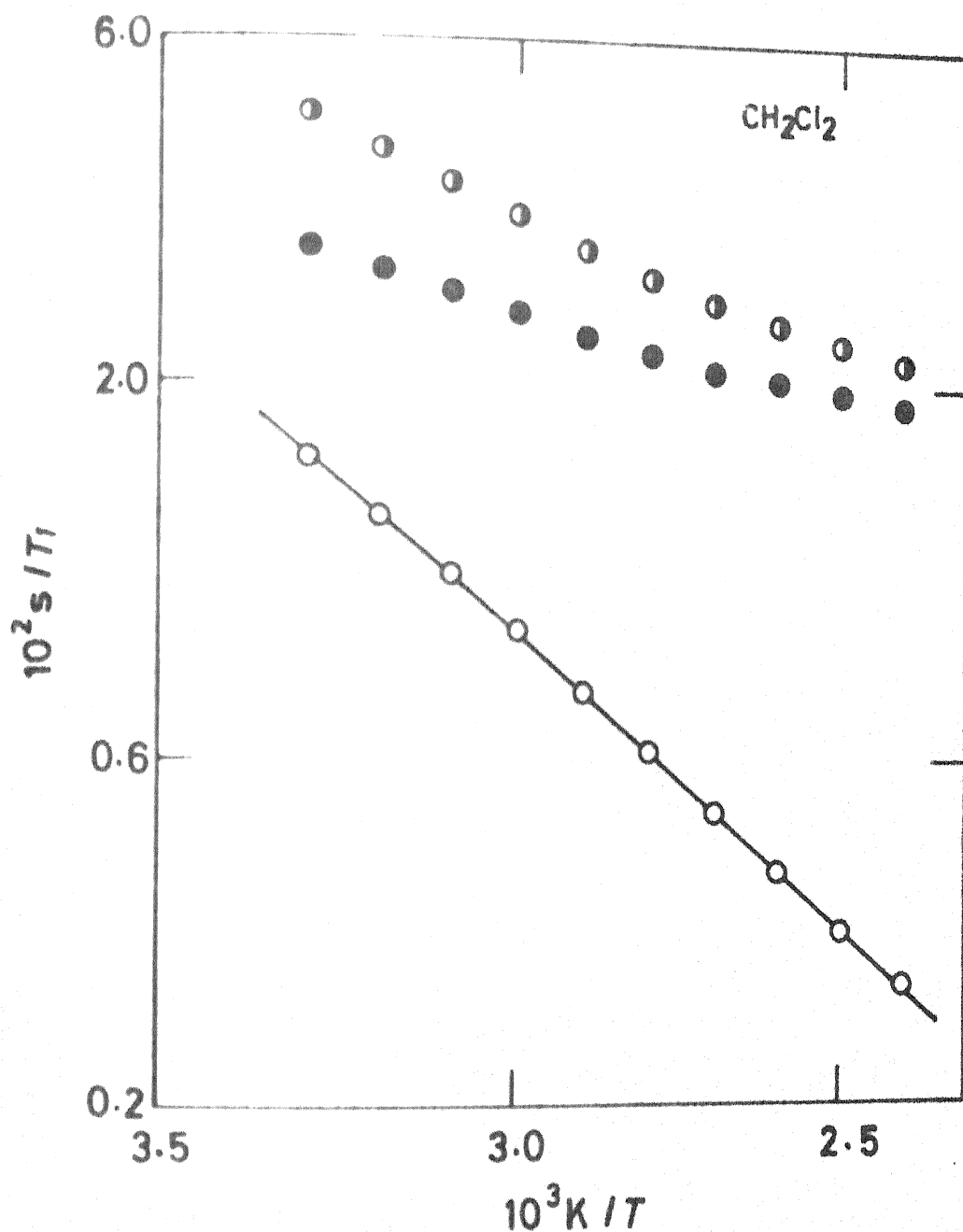
FIGURE 36. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN METHYLENE CHLORIDE. ⊙ , TOTAL RELAXATION RATE (OBSERVED). ○ , INTER-MOLECULAR RELAXATION RATE (CALCULATED). ● ,INTRA-MOLECULAR RELAXATION RATE.
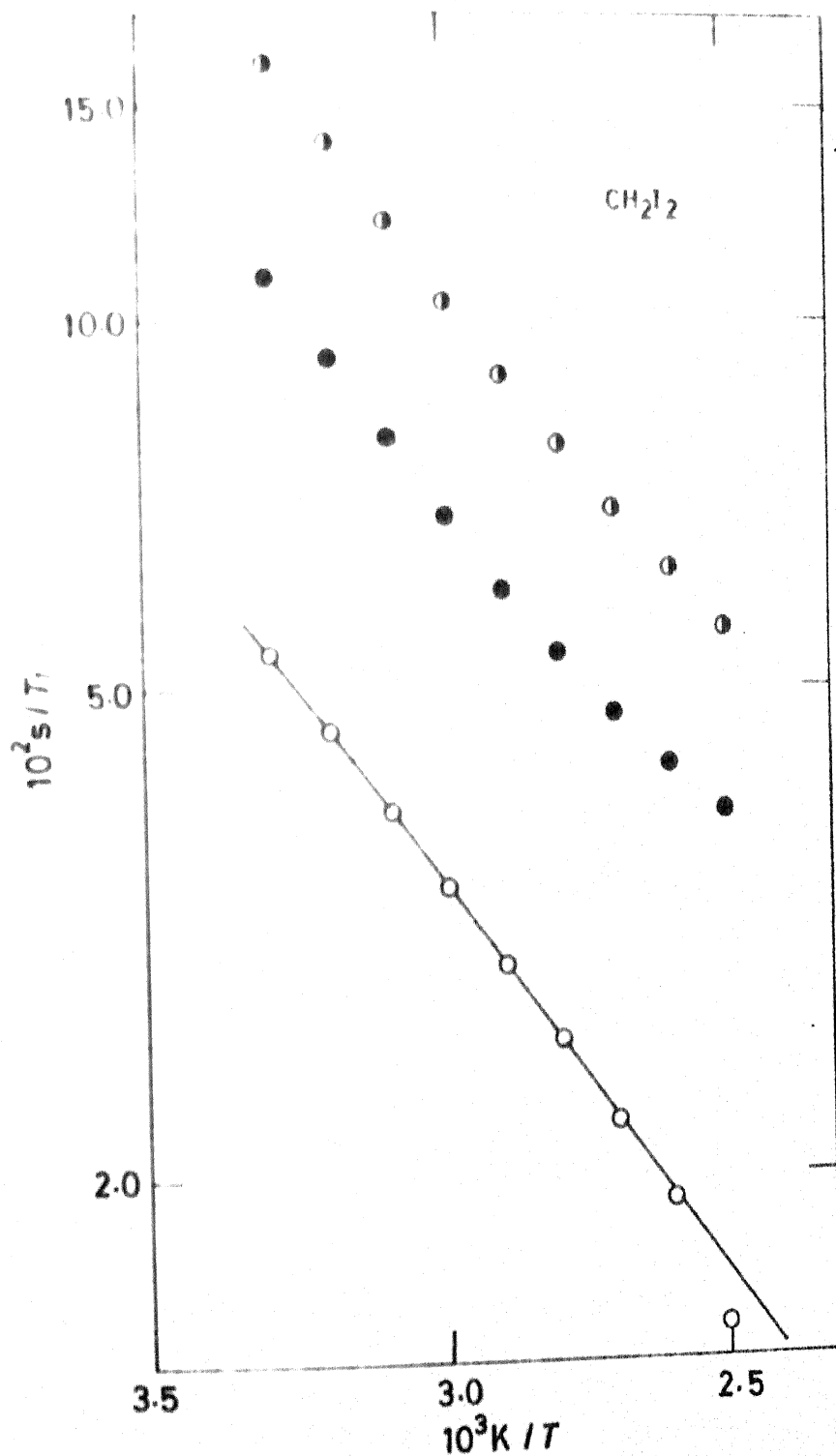
FIGURE 37. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN METHYLENE IODIDE. ◐, TOTAL RELAXATION RATE (OBSERVED). ○, INTERMOLE-CULAR RELAXATION RATE (CALCULATED). ●, INTRA-MOLECULAR RELAXATION RATE.
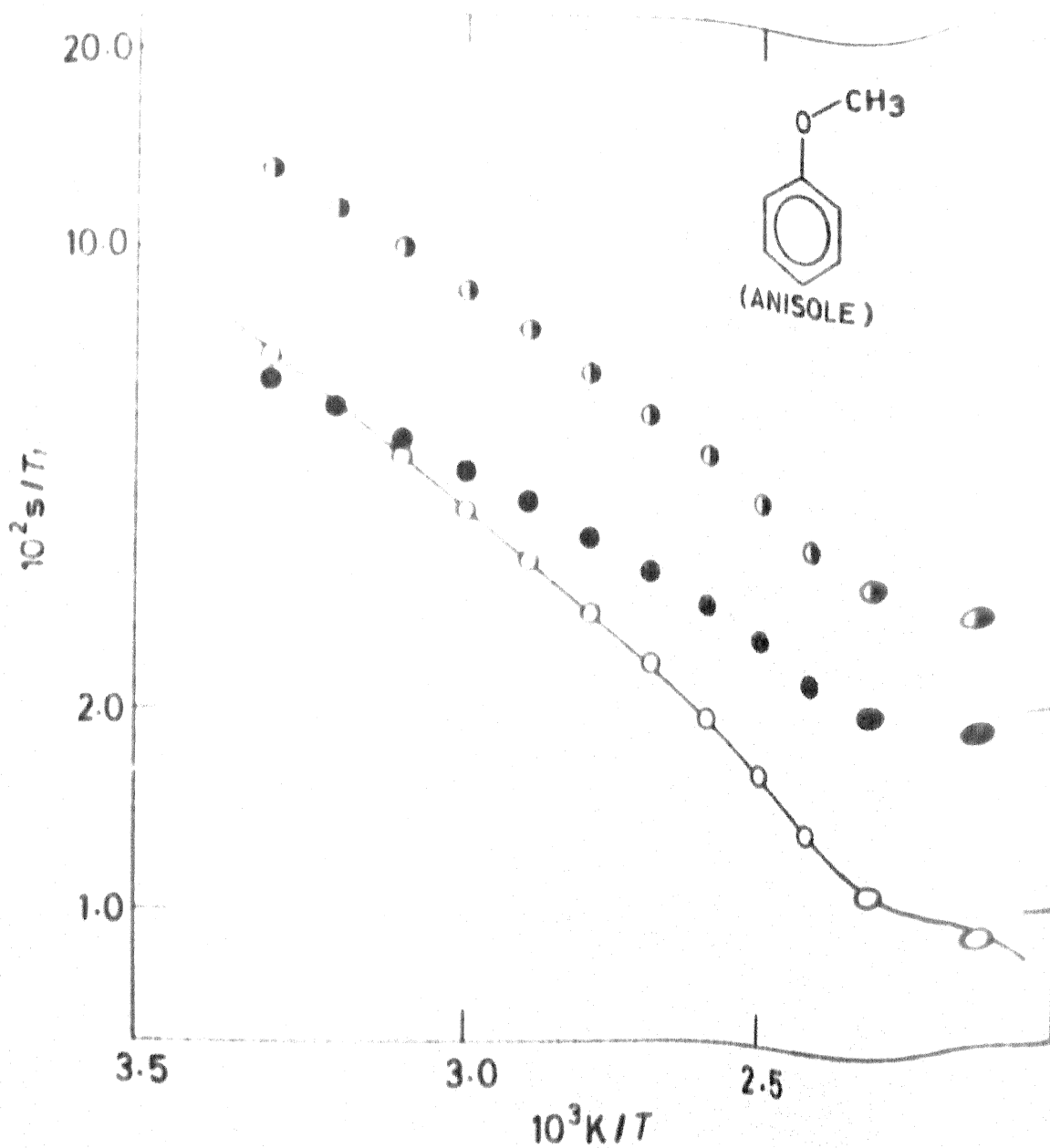
FIGURE 38. PLOTS OF THE VARIATION OF THE VARIOUS RELAXATION RATES WITH TEMPERATURE IN ANISOLE. ◑, TOTAL RELAXATION RATE (OBSERVED). ○, INTERMOLECULAR RELAXATION RATE (CALCULATED). ●, INTRAMOLECULAR RELAXATION RATE.

the intramolecular spin-rotational interaction whose strength increases with temperature rise. In anisole (Fig. 38) although the inter- and intramolecular relaxation rates are close at room temperature, they widen out with temperature rise, with intramolecular relaxation rate dominating the relaxation more and more and decreasing more slowly than the intermolecular relaxation rate. The import of such an observation is that the intramolecular interaction is fairly strong and the reorientational motion is inertial in nature. Detailed discussions and analyses are relegated to the discussions on individual compounds.

Temperature variations of the derived parameters as described in pages 116 to 121 are also carried out in the present group of compounds. Wherever a fit to an Arrheniuslike relation is possible, the corresponding activation energy is given in Table 5.1. $T_1\rho\eta/T$ and $T_1\eta/T$ corresponding to the ^{19}F relaxation decrease spectacularly with temperature, as would happen in case of strong spin-rotation interaction. Tables 5.2 and 5.3 give the parameters as described in Chap. 1 (see pp. 121 to 124).

5.1 $CH_2C\ell_2$ and CH_2I_2

Each of these molecules is a two-spin system with possible H-Cℓ and H-I scalar coupling. Since the scalar coupling would not affect the relaxation rate (p. 38) the relaxation rate analysis is carried out ignoring it. The large asymmetry

TABLE 5.2

THE CORRELATION TIMES IN AN ASSORTED GROUP OF COMPOUNDS

Compound	$10^3 K/T$	$\tau_{\theta 2}$ eff $\times 10^{13} s^{-1}$	$\tau_{\theta 2}$ BPP $\times 10^{13} s^{-1}$	τ free av $\times 10^{13} s^{-1}$	Inertial $\tau_{\theta 2}$ av $\times 10^{13} s^{-1}$	Mod. Hill $\tau_{\theta 2}$ av $\times 10^{13} s^{-1}$
CH_2Cl_2	3.3	11.42	7.37	2.77	2.03	1.12
	2.4	6.96	2.72	2.36	1.73	0.40
CH_2I_2	3.3	40.40	135.40	3.52	2.58	4.91
	2.5	14.80	39.83	3.07	2.25	1.45
$C_6H_5OCH_3$	3.3	10.42	36.83	–	–	–
	2.2	3.08	5.60	–	–	–
$C_6H_5CF_3$	3.3	50.44	27.31	7.99	5.86	9.70
	2.3	20.40	5.55	6.67	4.89	1.97

TABLE 5.3

SOME MOLECULAR PARAMETERS IN A GROUP OF ASSORTED COMPOUNDS

Compound	$10^3 K/T$	χ_{eff}	$a_2^m(0)_{eff}$	$a_2^m(0)_{av}$	Dipole moment D^{-1}
CH_2Cl_2	3.3	4.1	2.88	1.9	1.85
	2.4	2.9	2.06	0.9	
CH_2I_2	3.3	11.5	8.0	26.8	1.1
	2.5	4.8	3.37	9.1	
$C_6H_5OCH_3$	3.3	-	-	-	1.16
	2.2	-	-	-	
$C_6H_5CF_3$	3.3	6.3	4.41	3.3	2.6
	2.3	3.1	2.14	1.5	

between the moment of inertia components (see p.135) of these molecules is interesting. Although I_A is much smaller than I_B and I_C ; I_B and I_C seem to be close. The farinfrared work of Evans and Myron (1976) shows CH_2Cl_2 to behave as a symmetric top molecule. Recently the depolarized Rayleigh and Raman scattering studies in liquid CH_2Br_2 by Wang, Jones and Christensen (1976) has shown the slip boundary condition to be tenable. These suggest *a priori* a good deal of rotational freedom at least in case of CH_2Cl_2 , the lightest of the trio (CH_2Cl_2 , CH_2Br_2 and CH_2I_2).

The self-diffusion coefficients fitted to an Arrhenius relation gives for CH_2Cl_2 $E(D)$ = 3.37 kcal/mole which is large compared to 2.12 kcal/mole obtained by Sandhu (1971) and 2.40 kcal/mole obtained by O'Reilly *et al* (1972), and that for CH_2I_2 $E(D)$ = 2.73 kcal/mole which is less in comparison to 3.29 kcal/mole obtained by Sandhu (1971). Each molecule of CH_2I_2 being much heavier than that of CH_2Cl_2 naturally gives a smaller D at room temperature. But the expectation that the self-diffusion of a heavier molecule of similar shape will have greater surrounding dependence, higher temperature sensitivity and large $E(D)$ as seen by Sandhu (1971) is not presently borne out in the studies of CH_2Cl_2 and CH_2I_2. Just as observed in CH_3CN (Chap. 4) the CH_2Cl_2 self-diffusion coefficient varies much faster with temperature than the corresponding η.

The observed relaxation rates, intermolecular relaxation rates obtained using Torrey's relation (Eq. 1.10) and the intramolecular relaxation rates as the difference between the preceding two are plotted in Figs 36 and 37. The effective reorientational correlation times obtained using Eq. 1.13 are plotted in Fig. 40 Whereas the slow variation of the intramolecular relaxation rate CH_2Cl_2 might suggest the presence of some rotational coherence and consequent contribution to the relaxation the fast variation of the intramolecular relaxation rate with temperature in the heavier CH_2I_2 absolves spin-rotation contributing meaningfully to relaxation. The τ_{θ_2} eff for CH_2I_2 is essentially the corresponding dipolar reorientational correlation time. It is seen from Fig. 40 that CH_2Cl_2 reorientational correlation time is smaller and varies slower than that of CH_2I_2 reminiscent of an inertial reorientation process. The effective χ for CH_2Cl_2 in Table 5.3 is less than 3 at the highest working temperature and could also suggest inertial motion. The fast, and almost identical variation of the relaxation rates with temperature in CH_2I_2 (Fig. 37) shows the reorientation and translation processes to be temperature dependent in a similar way, suggesting good translation-rotation coupling in the liquid phase of this heavy molecule.

The calculations of the overall rotational diffusion constant are presented in the Table App. 3. As against Heatley (1974)'s
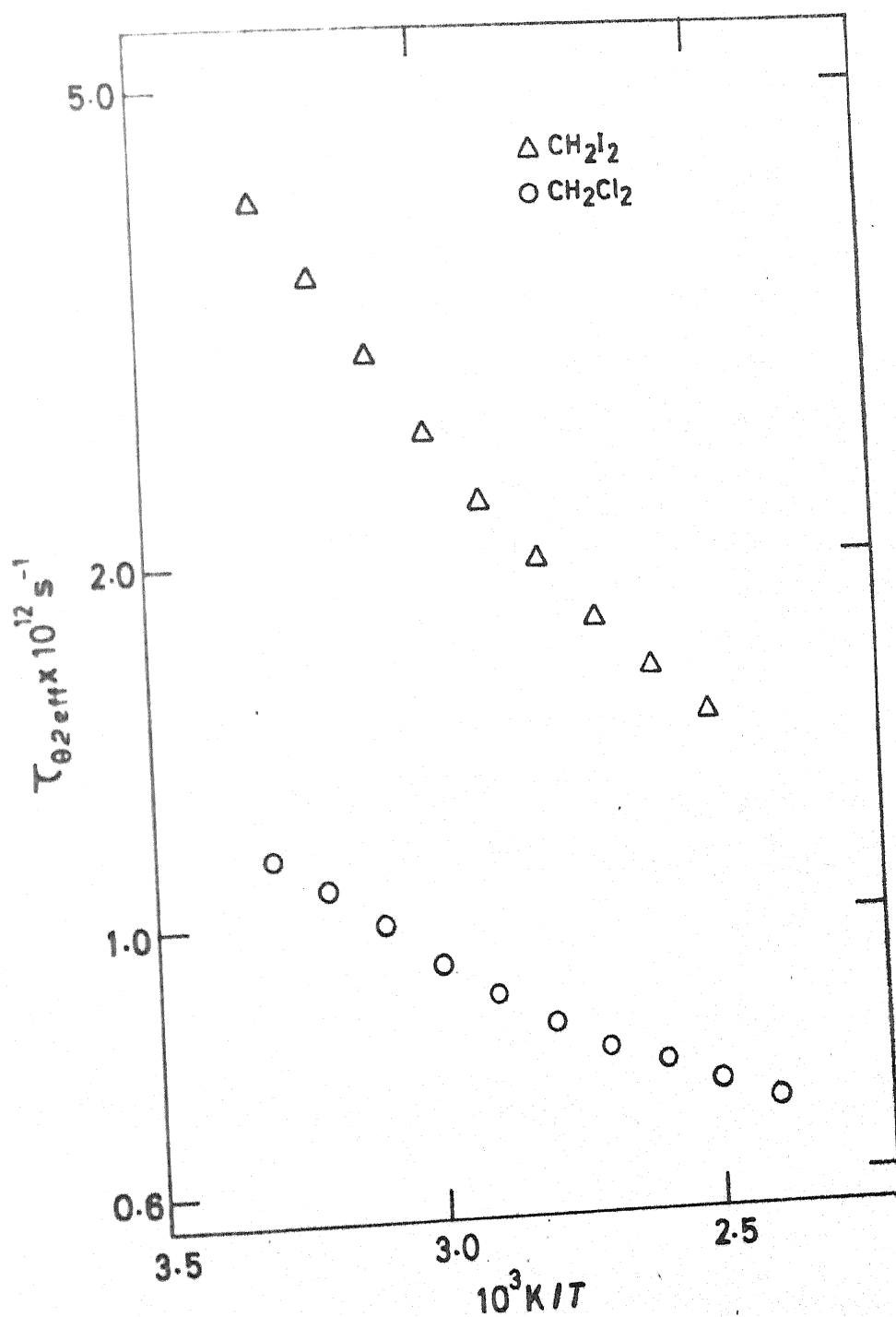
FIGURE 40 · PLOTS OF THE VARIATION OF THE EFFECTIVE REORIENTATIONAL CORRELATION TIMES ($\tau_{\theta 2\ eff}$) WITH TEMPERATURE IN METHYLENE CHLORIDE (O) AND METHYLENE IODIDE (△).

$D_{\perp} = 2.2 \times 10^{11} s^{-1}$ at normal room temperature the present calculation at room temperature gives $D_{\perp} = 2.18 \times 10^{11} s^{-1}$ with an Arrheniuslike activation energy 2.34 kcal/mole over the experimental temperature range. $D_{\parallel}$ calculated under the assumption of free parallel motion (see p.127) is $9.52 \times 10^{11} s^{-1}$ at room temperature which is much larger than the Heatley (1974)'s corresponding value of $4.4 \times 10^{11} s^{-1}$. The motion about the parallel symmetry axis in CH_2Cl_2 is therefore somewhere between free and diffusive but nearer the diffusive end whereas the motion about the approximate perpendicular symmetry axis is diffusive. In the light of this, it is fair to expect both the rotational motions about the approximate perpendicular and parallel symmetric axis in the heavier CH_2I_2 to be diffusive.

5.2 $C_6H_5OCH_3$

In anisole there are two distinct groups of proton containing species (C_6H_5 and CH_3). There could be intramolecular relative motion between the species and that CH_3 could be quite mobile. (It is unfortunate that the rotational parameters on the molecule could not be gotten as yet.) The overall relaxation has contribution from the two distinct groups and from the cross-correlation between the two. Cutnell *et al* (1975) have shown that at $10^3 K/T = 3.3$ the cross relaxation contribution to the total relaxation is 23.8% and decreases sharply with temperature reducing to 16% at $10^3 K/T = 3.0$. It can thus be assumed that at our highest working temperature ($10^3 K/T = 2.2$) the cross relaxat

contribution is negligibly small. It is also seen by Cutnell *et al* that the CH$_3$ group relaxation rate is the more dominant one. The present work provides complementary D data and takes a look into the problem of analysis of the T_1 and D data in a somewhat simplified way.

The measured self-diffusion coefficients could be fitted to an Arrheniuslike relation (Fig. 33) which gives an activation energy 3.29 kcal/mole (Table 5.1). The observed overall ^{1}H relaxation seems to be exponential in time thus showing, if any, small effect due to cross relaxation. Also in the work of Cutnell *et al* (1975) an almost similar variation of the overall proton relaxation rates in CH$_3$ and C$_6$H$_5$ could help make such a contention. (Actually the slightly weaker variation of the -CH$_3$ proton relaxation rate with temperature might be because of a lesser dependence on the surrounding which might suggest an internal motional freedom.) The activation energy of the observed total relaxation rate agrees well with the value 2.77 kcal/mole obtained by Cutnell *et al* (1975). The intermolecular relaxation rate over the experimental temperature range are estimated using Eq. 1.10. The total relaxation rate, intermolecular relaxation rate, and the intramolecular relaxation rate as the difference between the previous two rates are plotted in Fig. 38. The intramolecular relaxation rate although comparable to the intermolecular relaxation rate at room temperature decreases comparatively slowly with temperature increase. The activation

energies of the inter- and intramolecular relaxation rates
are 3.59 and 2.23 kcal/mole respectively (Table 5.1). This
suggests that the intramolecular relaxation to be a temperature
activated process of lesser strength than the intermolecular
relaxation rate. Further analysis of the intramolecular relaxa-
tion rate is based on Gutowsky and Woessner (1956)'s relation,

$$R_{1intra} = 3/2 \, \gamma^4 \hbar^2 (N_{C_6H_5}^{-1} \Sigma \hbar_{ij}^{-6} + N_{CH_3} \Sigma \hbar_{k\ell}^{-6}) \tau_{\theta_2 \, eff} \qquad (5.1)$$

where N is the number of resonating spins in the corresponding
species subscripted to N, $\hbar_{ij}$ and $\hbar_{k\ell}$ are the separation between
the protons in C_6H_5 and CH_3 groups respectively. Since $\hbar_{ij}$s
for the ortho, meta and para protons are respectively 2.44, 4.23
and 4.88 Å and $\hbar_{k\ell} = 1.78$ Å, the first term within the bracket of
the foregoing relation (Eq. 5.1) is about 11% of the total.
It is, therefore, essentially the CH_3 group motion which
determines the ^1H intramolecular relaxation. An effective
correlation time defined by Eq. 5.1 is evaluated (Table 5.2).
The $\tau_{\theta_2 \, eff}$ seems to be lesser than $\tau_{\theta_2 \, BPP}$ where the later is
an underestimated value (because of the use of small Stokes-
Einstein radius, see Appendix) which might suggest a freer
reorientational motion arising because of the possible CH_3 rotati

5.3 $C_6H_5CF_3$

An early work on α-trifluoro toluene was made by
Green and Powles (1965). In the present work apart from
measuring the ^1H and ^{19}F relaxation times the complementary

self-diffusion coefficients are measured from room temperature to about 180 °C. The relaxation times seem to agree well with those reported by Green and Powles (1965). A fit of the diffusion data to an Arrhenius relation (Fig. 34) gives an activation energy 2.77 kcal/mole. The observed relaxation seems to be exponential in time and it is assumed that all the protons relax identically. The intermolecular relaxation rates are as usual evaluated using the Torrey's relation (Eq. 1.10) for both ^{1}H and ^{19}F. The intramolecular relaxation rates are obtained as the difference between the total and intermolecular relaxation rates. All these relaxation rates are plotted in Fig. 39. For ^{19}F relaxation the intramolecular interaction seems to almost completely determine the total relaxation rate. The large value and fast increase of the ^{19}F intramolecular relaxation rates seem to be completely due to the spin-rotation interaction. The rotational coherence giving rise to such large ^{19}F spin-rotational relaxation could not be because of overall rotational coherence and arises due to the persistence of the rotation of the facile CF$_3$ group. Further, the strong temperature dependence of the ^{19}F intramolecular relaxation rate suggests a temperature activated rotational process but not a free rotation which is weakly temperature sensitive.

The proton intramolecular relaxation rate steadily decrease with temperature increase suggesting to be arising due to intra-molecular dipolar interaction. As in anisole (p.156) the

Gutowsky and Woessner relation (Eq.5.1) is used for the C_6H_5 group to determine the proton effective reorientational correlation time. The correlation times and other parameters are usual presented in Table 5.2 and 5.3 where χ_{eff} corresponds to ^1H. The large reorientational correlation time is clearly suggestive of a diffusive process determining the ^1H relaxation.

orientational changes would arise simultaneously. Molecular asymmetry, translation-rotation coupling and diffusive motions seem to go on hand in hand. Although the translational motion seems to be mostly diffusional, the orientational motions are often unexpectedly inertial in somewhat heavy but asymmetric molecules. In the case of inertial molecular dynamics the motion is mostly characterised by the moment of inertia and mass of the molecule and is less mindful of the surrounding molecules. Since, in the type of temperature variation work presented here, the molecular kinetic energy and packing are greatly affected and molecular surroundings have little effect on the inertial molecular dynamics, the analogous parameters have little temperature sensitivity and viscosity dependence.

The aim of this work has been to separate the translation, orientation and rotation dependent parameters as functions of temperature. In order to do this, a good estimation of the molecular dimension is necessary. In liquids the picture of the average molecular radius is particularly hazy. There seem to be many approaches for such estimations found suitable for a variety of cases (Appendix). The best course, from the point of view of the analysis of the nmr dynamical parameters, is felt to be through the estimation of the Stokes-Einstein radius. The molecular radius thus obtained is smaller than those obtained through molecular models but obviates the need for micro-viscosity correlations necessary for such molecular motion in

its own surrounding, and is also in agreement with some other work as stated in the Appendix. Using the D measured *in situ* and available viscosity data over the experimental temperature range, the average Stokes-Einstein molecular radius for the molecule is obtained. Although the best method to determine the intermolecular relaxation is through the measurement of T_1 as a function of concentration in its isotopic analogue, Torrey's relation for the intermolecular relaxation rate in conjunction with the Stokes-Einstein radius gives good estimates of such relaxation rates. This method obviates the dubious procedure of the consideration of hexagonal close packing of molecules in liquids and the simultaneous use of microviscosity correction factors to make the relaxation rate estimates reasonable. The separated intramolecular relaxation rate has contributions from both orientational changes and rotational motion of the molecule. Although a constant density T_1 and D measurement could have been more informative such temperature variation work as presented in this thesis nevertheless gives valuable information about the molecular dynamics.

The coherent pulsed nmr assembly for such temperature variation work as reported here gives good T_1 and D data with an error ± 5%. With the help of the available density and the coefficient of viscosity data over the experimental temperature range, and moments of inertia, the various derived parameters and correlation times obtained give valuable information

about the molecular dynamics. The dipole moments of some of these molecules though quite large, have seemingly little effect on the dynamics. It is mainly the molecular shape which determines the dynamics.

The methyl group of compounds are particularly interesting because of the rotational freedom about the axis joining the CH_3 group to the molecular skeleton. In the study of symmetric top CH_3I and CH_3CN molecular liquids over the experimental temperature range (room temperature to about 140 ^{O}C) large spin-rotational contributions to relaxation are observed. The possibility of rotational freedom about the molecular symmetry axes is responsible for this. The rotational motion about an axis perpendicular to the symmetry axis is, however, diffusiona The study in the highly polar CH_3NO_2 (over the temperature range room temperature to about 130 ^{O}C) shows the intramolecular interaction relaxation contribution to total relaxation getting more and more important with temperature rise. As CH_3NO_2 is highly polar and would in the liquid phase give rise to a local structure, such a local structure does not seem to affect the reorientational coherence. In acetone the study over the temperature range, room temperature to about 130 ^{O}C, shows reorientational coherence which could be because of the intra-molecular methyl group rotation. Dimethyl sulfoxide, although structurally close to acetone, seems to have a diffusive reorientational motion over the temperature range, room ter ture to nearly 180 ^{O}C. Also a good translation-rotation

coupling ensues. Although CH_2Cl_2 is an asymmetric molecule, interestingly enough it exhibits a good amount of reorientational coherence over the experimental temperature range- room temperature to about 140 $^{\circ}$C. This, however, does not happen in the structurally similar but bulkier CH_2I_2 over the same temperature range. In addition, in the molecular dynamics of methylene iodide a good amount of translation-rotation coupling is present. A noteworthy observation in CH_2Cl_2 molecular dynamics is that although the rotational motion about the perpendicular symmetry axis is diffusive, such a motion about the parallel symmetry axis though not inertial is seemingly somewhat closer to the diffusive limit. The work in anisole over the temperature range room temperature to 210 $^{\circ}$C is analysed in a particularly simplified way. In view of the small cross-correlation effects in the overall ^1H relaxation in this molecule and the earlier reported almost similar variation of the C_6H_5 and CH_3 ^1H spin-lattice relaxation times, the use of D measured *in situ* is particularly rewarding. The ^1H relaxation is dominated by the intramethyl group interaction but the effect of somewhat more facile CH_3 group motion is evident from the intramolecular relaxation rate. α-trifluoro toluene has the facile intramolecular CF_3 group rotation giving rise to the most dominant spin-rotation interaction contribution of the ^{19}F relaxation. The temperature variation of the ^{19}F intramolecular relaxation over the temperature range, room temperature to about 160 $^{\circ}$C, however, hints at a temperature activated CF_3 group rotation.

The reorientation of the C_6H_5 is diffusive which is shown to be so through the ^1H relaxation.

In obtaining further detailed information about the molecular dynamics a more rewarding picture will be obtained on the following lines. T_1, D data at constant density will be quite revealing and for that matter pressure variation work need be incorporat Relaxation studies on more than one spin bearing different structural symmetries within the molecule will better reflect the molecular rotational asymmetric motions. The sister branches of studies such as light scattering, neutron scattering, dipole relaxation etc. need be combined to get a comprehensive picture of the molecular dynamics in the molecular liquids. Since the measurement of spin-rotational interaction seems to be a special feature of nmr a study over the largest possible liquid-vapour coexistence range will be rewarding. Although description of either of the limits of molecular dynamics could be easily made a successful attempt to encompass the entire range is lacking. Molecular dynamics in polar liquids as well as solution studies are gradually engaging more and more attention.

APPENDIX

ON THE ESTIMATION OF MOLECULAR RADIUS AND DIFFUSION COEFFICIENTS IN MOLECULAR LIQUIDS

The generalized Einstein diffusion coefficient relates the diffusion coefficient D to the coefficient of friction ζ through the relation

$$D = kT/\zeta . \qquad (A.1)$$

For spherical bodies the Stokes relations for the translational and rotational friction are respectively,

$$\zeta_{trans} = 6\pi\eta a^3, \qquad (A.2)$$

$$\text{and } \zeta_{rot} = 8\pi\eta a^3 . \qquad (A.3)$$

Einstein used these macrobody friction coefficients for microbody molecular motions. The consequent mathematical relationships between the diffusion coefficients, moleculr radius, viscosity and temperature is known as the Stokes-Einstein relation. The questions are how far such an approximation is correct and what a is to be taken for the molecules. It is argued in the following that the hydrodynamical relationship is valid, provided not much physical significance is attached to the molecular radius values. The molecular radii of approximated hardspherical bodies are merely artifacts to get agreeable numerical values for dynamical paramete It is also pointed out that such a course imbibes less number of approximations than the other methods for finding a.

The methods under discussion for finding a are :
(1) the hexagonal close packing of molecules in liquid,
(2) the van der Waals volume of the molecule, (3) the
Lennard-Jones separation for minimum mutual potential
energy, and (4) the Stokes-Einstein relation.

In the hexagonal close packing model of the liquid,
spheres approximated for molecules are imagined to hexago-
nally close pack the lattice. The molecular radius a_{HCP}
is then obtained using the relation

$$4/3 \; \pi a_{HCP}^3 = 0.74 \; M_r/\rho N_A \qquad (A.4)$$

where M_r is the molecular weight of the compound, ρ is
the density of the liquid, and N_A is the Avogadro constant.
The validity of such a relation over the entire liquid
phase and for all types of non-spherical molecules is suspect.
To amend for the expected discrepancy between the theoretical
and experimental diffusion coefficients microviscosity
correction factors (Gierer and Wirtz (1953)) are used (p.40). Thus
the diffusion coefficients are given by

$$D_{trans} = kT/6\pi\eta a_{HCP}\mu_t \; , \qquad (A.5a)$$
$$D_{rot} \;\; = kT/8\pi\eta a_{HCP}^3\mu_r \; , \qquad (A.5b)$$

where, for neat liquids, μ_t the translational microviscosity
factor is 0.5 and μ_r the rotational microviscosity factor
is 1/6.125 ($\approx$ 0.163).

The van der Waals incremental volumes (Edwards (1970))
for the constitutents of the molecules are also used to estimate
the molecular volume and then the equivalent spherical molecular
radius. Such a van der Waals molecular radius is given by

$$4/3 \; \pi a_W^3 = V_W \; .$$ (A.6)

Lennard-Jones parameters provide a rough picture of
the liquid state as well. Svehla (1962) lists the low
velocity collision diameters (which is the distance at
which the intermolecular potential vs separation changes
sign, attractive to repulsive and $vice \; versa$). Half of
this collision diameter is taken to be the Lennard-Jones
radius a_W in the present discussion.

The fourth and seemingly the least cumbersome way of
finding the molecular radius is through the validity of
the Stokes-Einstein relation. Experimental values of $\mathcal{D}$
and η are used to find $\mathcal{D}\eta/T$ at several sample temperatures.
The Stokes-Einstein relation for the translational
diffusion gives,

$$\mathcal{D}\eta/T = k/6\pi a \; .$$ (A.7)

The constancy of $\mathcal{D}\eta/T$ over the working temperature range
is a pointer towards the validity of the hydrodynamic
relation for the translational motion. The values of $\mathcal{D}\eta/T$
at different temperatures for several compounds are listed

in Table App. 1.   The near constancy of $\mathcal{D}\eta/T$ over the working temperature range helps finding the Stokes-Einstein molecular radius a_{SE} using

$$a_{SE} = k/6\pi(\mathcal{D}\eta/T)_{av} \qquad (A.8)$$

where $(\mathcal{D}\eta/T)_{av}$ is the average value of $\mathcal{D}\eta/T$ over the working temperature range.

The molecular radii obtained by the aforementioned four different ways are listed in Table App. 2. It is seen that for every molecule under consideration a_{HCP} gives the largest and a_{SE} the smallest molecular radius value. The ratio (a_{SE}/a_{HCP}) and $(a_{SE}/a_{HCP})^3$ are also listed in the Table App. 2. a_{SE} is found to be about half of a_{HCP} for each molecule. The average a_{SE}/a_{HCP} and $(a_{SE}/a_{HCP})^3$ for the series of compounds are 0.539 and 0.165 respectively. It therefore appears that instead of using the hexagonal close packing and microviscosity factors to maintain the diffusion coefficient and a_{HCP} relation (Eqs. A.4, A.5a and A.5b) one can straight away use the Stokes-Einstein relations (Eqs. A.1, A.2 and A.3) to find a. The success of this procedure depends on the validity of the Stokes-Einstein relation whereas the hexagonal close packing method, in addition, assumes hexagonal close packing of molecules in the liquid phase and also a microviscosity model. Nevertheless the Stokes-Einstein relation is shown to be valid in the liquid phase quite well. (Flowers and Mendoza (1970)).

THE EXPERIMENTAL VALUES OF Dn/T AT DIFFERENT TEMPERATURES FOR VARIOUS COMPOUNDS

COMPOUND	$10^{14} \times Dn/T$ m^{-2} s P^{-1} K, at 10^3 K/T =													
	3.4	3.3	3.2	3.1	3.0	2.9	2.8	2.7	2.6	2.5	2.4	2.3	2.2	2.1
Water	–	6.58	6.76	7.05	7.28	7.73	8.11	8.69	9.10	–	–	–	–	–
Benzene	–	4.29	4.28	4.26	4.21	4.18	4.15	4.24	4.03	3.83	3.91	3.83	3.76	–
CH_3I	–	5.01	5.12	5.20	5.31	5.39	5.48	5.52	5.60	5.66	–	–	–	–
CH_3CN	–	5.77	6.17	6.57	6.99	7.41	7.99	8.43	8.95	9.61	10.28	10.88	–	–
CH_3NO_2	–	4.38	4.46	4.51	4.60	4.69	4.74	4.79	4.82	4.85	4.86	–	–	–
CH_3COCH_3	–	4.63	4.69	4.67	4.66	4.68	4.65	4.64	4.68	4.58	–	–	–	–
CH_3SOCH_3	–	5.34	4.86	4.50	4.14	3.93	3.73	3.55	3.59	3.62	3.74	3.83	4.01	–
CH_2Cl_2	–	4.56	4.83	5.12	5.42	5.76	6.07	6.37	6.71	7.06	7.38	–	–	–
CH_2I_2	–	4.47	4.37	4.25	4.15	4.04	3.98	3.97	3.96	3.95	–	–	–	–
Anisole	4.79	4.82	4.84	4.83	4.82	4.79	4.76	4.76	4.72	4.70	4.61	4.57	4.51	4.44
$C_6H_5CF_3$	–	4.45	4.46	4.50	4.49	4.47	4.37	4.34	4.15	3.95	3.75	3.42	–	–

TABLE IPP. 2

COMPARISON OF MOLECULAR RADII OF SEVERAL COMPOUNDS BY VARIOUS METHODS

Compound	a_{HCP}/Å	a_w/Å	a_{LJ}/Å	a_{SE}/Å	(a_{SE}/a_{HCP})	$(a_{SE}/a_{HCP})^3$
Water	1.74	1.70	1.32	0.95	0.546	0.163
Benzene	2.96	2.68	2.67	1.79	0.605	0.221
CH_3I	2.63	2.37	2.12	1.38	0.525	0.145
CH_3NO_2	2.51	2.11	–	1.52	0.625	0.244
CH_3CN	2.49	2.24	2.30	0.90	0.361	0.047
CH_3COCH_3	2.78	2.49	–	1.57	0.565	0.180
CH_3SOCH_3	2.80	–	–	1.80	0.643	0.266
CH_2Cl_2	2.65	2.38	2.45	1.24	0.468	0.102
CH_2I_2	2.87	2.70	2.58	1.77	0.617	0.235
Anisole	3.18	2.94	–	1.55	0.487	0.115
Thiophene	2.85 [1]	2.57	–	1.58	0.554	0.170
1,2 Dichloroethane	2.85 [1]	2.34	–	1.39	0.488	0.116
$C_6H_5CF_3$	3.30	2.99	–	1.74	0.529	0.148

[1] Kitchlew (1971)

One important thing to note here is that as the intermolecular relaxation rate due to Torrey (1953) $R_{1 inter}$ is proportional to aD,

$$(R_1)_{inter} = \pi \gamma^4 \hbar^2 N_A n\rho / 5M_h aD$$

and as a bears an inverse relation to D (Eq. A.7), the error in estimating a through D measurement and the use of the Stokes-Einstein relation however does not affect the $(R_1)_{inter}$ estimation. Inspite of the small a_{SE} the validity of the hydrodynamic relation and the correct estimation of $(R_1)_{inter}$ are quite heartening.

van Loef (1975) shows that for neat molecular liquids the packing fraction ranges from 0.465 to 0.52. Parkhurst and Jonas (1975) also show that for benzene the packing fraction is 0.493. The use of such a smaller than the hexagonally close packing fraction (0.74) will predict more agreeable diffusion coefficients. All these works advocate for an a shorter than a_{HCP}. The work of McCool, Collings and Woolf (1972) in benzene over a temperature range 15°C to 50°C at a pressure 1.01N/m gives an average $a = 1.63$Å which compares favourably with the value 1.79Å obtained in the present work (Table App. 1). Although water, due to association, is fairly difficult to be understood, the contentions of Rahman and Stillinger (1971), and Walford, Clarke and Dore (197 that the water molecules can be approximated to spheres of 1Å

radius is also borne out by our Stokes-Einstein radius of 0.95 Å (see Table App. 2).

It is worthwhile chronicling two other approaches in reducing the Debye correlation time estimates or the molecular radius to explain the observations. The mutual viscosity model of Hill (1954) shows that the hydrodynamic estimates of reorientation correlation times need to be reduced to 1/5 the value, and 1/5 compares favourably to our average $(a_{SE}/a_{HCP})^3 = 0.539$. Longuet-Higgins and Pople (1956) show that the hard sphere radius is 9/5 times the Stokes-Einstein radius for consistency between the hard sphere thermodynamic model and the hydrodynamic result which also compares favourably with $a_{HCP}/a_{SE} = 0.165$.

As mentioned in Chapter 1 (p.42) the translation-rotation coupling parameters is large ($\kappa \sim 1$), when the anisotropic part of the intermolecular potential is large and the translation-rotation coupling is small ($\kappa \ll 1$) for very weakly anisotropic potentials. κ calculated using Eq. 1.25, at the highest and the lowest working temperatures in some of the presently investigated molecular liquids where the intramolecular dipolar interaction is strong enough to determine the total intramolecular relaxation are as follows:

Compound	$10^3 K/T$	κ	$10^3 K/T$	κ
CH_3COCH_3	3.3	0.753	2.5	1.511
CH_3SOCH_3	3.3	0.357	2.2	0.317
$CH_2C\ell_2$	3.3	0.669	2.4	0.390
CH_2I_2	3.3	0.298	2.5	0.372
$C_6H_5OCH_3$	3.3	0.240	2.2	0.549
$C_6H_5CF_3$	3.3	1.846	2.3	3.679

Molecules with large spin-rotation interaction give rise
to a $\tau_{\theta 2}$ eff larger than actual $\tau_{\theta 2}$ corresponding to the intra-
molecular dipolar interaction. This yields a large κ which
might mislead in suggesting a good translation-rotation coupling.
The high temperature κ value in CH_3COCH_3 is a case to the point.
Although ample of translation-rotation coupling and large κ in
$C_6H_5CF_3$ motion is expected the κ values are found to be little
too large (greater than 1) which is little disconcerting. The
reason could lie in our ^1H intramolecular dipolar relaxation
rate estimation (and the consequent $\tau_{\theta 2}$ value) being about
two times larger than the values reported by others (Bull and
Jonas (1970)).

The methods to theoretically estimate the translational
and rotational diffusion coefficients in molecular liquids are
described in the following. The Stokes-Einstein radius a_{SE}
obtained from measurements (Table App. 2) can be directly

used in the Debye relation (Eq. 1.11) and

$$\mathcal{D}_{rot} = 1/6\tau_\theta \qquad\qquad (A.9)$$

(see Abragam (1961)), to give the $\mathcal{D}_{rot}$ which are presented under $\mathcal{D}_{rot\ SE}$ in Table App. 3. Relations given by Eqs. A.5a and A.5b along with the translational and rotational micro-viscosity factors given in p.168 are used to calculate the translational and rotational diffusion constants listed under the legend HCP *cum* μvisc in Table App. 3. Notwithstanding the limitation of the cubic cell model in treating the translation motion alone (Houghton (1964)) the self-diffusion coefficient predictions thereof are very good. The results presented in Table App. 3 are obtained using the relation

$$\mathcal{D} = RT\rho\nu^{2/3}/6\eta M_r , \qquad\qquad (A.10)$$

where the cube volume ν assigned to each molecule is

$$\nu = M_r/N_A\rho ,$$

and other parameters have their usual meaning. The translational diffusion coefficients measured *in situ* are also presented in Table App. 3. All the mentioned $\mathcal{D}_{trans}$, $\mathcal{D}_{rot}$ calculations pertain to the temperature $10^3 K/T = 3.3$. The rotational diffusion constant available for some of the compounds are quoted in the last column of the Table App. 3.

The agreement between the diffusion coefficient values theoretically estimated and experimentally determined is quite

DIFFUSION COEFFICIENTS IN SOME MOLECULAR LIQUIDS

Compound	Cubic Cell, $D_{trans} \times 10$ m² s	HCP cum μvisc. $D_{trans} \times 10^9$ m² s	Exptl. $D_{trans} \times 10^9$ m² s	D_{rot}-SF $\times 10^{-11}$ s	HCP cum μvisc. $D_{rot} \times 10^{-11}$ s	Other reported $D_{rot} \times 10$
H_2O	2.58	3.14	2.46	2.36	2.30	
C_6H_6	2.21	2.54	2.15	0.49	0.66	$1.17^a, 1.07^b, 1.1^c, 1.4^d$
CH_3I	3.00	3.64	3.30	1.37	1.19	$1.35^e, 1.4^f, 1.5^d, 1.51^b, 1.$
CH_3CN	4.32	2.57	5.05	6.51	1.89	
CH_3NO_2	2.49	3.00	2.30	0.74	1.09	
CH_3COCH_3	4.56	5.32	4.71	1.43	1.56	1.6^g
CH_3SOCH_3	0.65	0.80	0.80	0.14	0.24	0.35^g
CH_2Cl_2	3.51	4.10	3.41	2.23	1.32	2.2^c
CH_2I_2	0.56	0.64	0.56	0.12	0.18	
$C_6H_5OCH_3$	0.98	1.42	1.49	0.45	0.32	
$C_6H_5CF_3$	2.21	2.60	2.62	0.61	0.55	

[a]Gillen et al (1971), [b]Griffiths (1973), [c]Heatley (1974), [d]Lyerla and Levy (1974), [e]Bopp (19..), [f]Zeidler (1971), [g]Lyerla and Grant (1972).

good in all except the linear molecule CH_3CN . It could also be seen from Table App. 3 that this fast variation of D compared to η (see the corresponding activation energies in Table 4.1) gave rise to a large variation of $D\eta/T$ over the temperature range and a quite small a_{SE} compared to CH_3I etc.. Assuming CH_3CN molecular radius to be same as the CH_3I radius (1.38 Å) the calculated value of HCP cum μvisc. D_{trans} is $5.14 \times 10^{-9} m^2 s^{-1}$ and $D_{rot\ SE}$ is $1.82 \times 10^{11} s^{-1}$ which compare favourably with the respective experimental values: $5.08 \times 10^{-9} m^2 s^{-1}$ and $1.89 \times 10^{11} s^{-1}$.

It suffices to conclude that if the Stokes-Einstein radii for the molecules are consistently used in the Torrey's relation for the intermolecular relaxation rates and the Debye's relation for the rotational diffusion constants, agreeable estimates of the corresponding parameters are obtained.

- * -

Bliss was it in that dawn to be alive
—Wordsworth

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